The Chloronium Cation \([\text{(C}_2\text{H}_3)_2\text{Cl}^+]\) and Unsaturated C\(_4\)-Carbocations with C=C and C≡C Bonds in Their Solid Salts and in Solutions: An \(\text{H}^1/\text{C}^{13}\) NMR and Infrared Spectroscopic Study

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Abstract: Solid salts of the divinyl chloronium \((\text{C}_2\text{H}_3)_2\text{Cl}^+\) cation (I) and unsaturated \(\text{C}_4\text{H}_7^+\) and \(\text{C}_4\text{H}_7^+\) carbocations with the highly stable \(\text{CHB}_{11}\text{Hal}_{11}^-\) anion (\(\text{Hal}=\text{F, Cl}\)) were obtained for the first time. At 120 °C, the salt of the chloronium cation decomposes, yielding a salt of the \(\text{C}_4\text{H}_7^+\) cation. This thermally stable (up to 200 °C) carbocation is methyl propargyl, \(\text{CH}≡\text{C}^+\text{H}-\text{CH}_3\) (VI), which, according to quantum chemical calculations, should be energetically much less favorable than other isomers of the \(\text{C}_4\text{H}_7^+\) cations. Cation VI readily attaches HCl to the formal triple \(\equiv\text{C}\) bond to form the \(\text{CHCl}≡\text{CH}\text{H}-\text{CH}_3\) cation (VII). In infrared spectra of cations I, VI, and VII, frequencies of \(\text{C}≡\text{C}\) and \(\equiv\text{C}\) stretches are significantly lower than those predicted by calculations (by 400–500 cm\(^{-1}\)). Infrared and \(^{1}\text{H}/^{13}\text{C}\) magic-angle spinning NMR spectra of solid salts of cations I and VI and high-resolution \(^{1}\text{H}/^{13}\text{C}\) NMR spectra of VII in solution in \(\text{SO}_2\text{ClF}\) were interpreted. On the basis of the spectroscopic data, the charge and electron density distribution in the cations are discussed.

Keywords: chloronium cation; vinyl and propargyl carbocations; magic-angle spinning NMR measurements

1. Introduction

Simple saturated carbocations (\(\text{C}_2–\text{C}_7\)) have been studied experimentally in condensed phases [1–7] and their infrared (IR) spectra have been interpreted [6–8]. Protonated arenium cations, starting with \(\text{C}_6\text{H}_7^+\), have been broadly studied by NMR spectroscopy in liquid superacids and as carborane salts [9,10]. There are more problems with the research on unsaturated nonarenium carbocations, because their salts have not been obtained so far. The simplest and least stable vinyl cation, \(\text{C}_2\text{H}_3^+\), and isomers of \(\text{C}_3\text{H}_5^+\) and \(\text{C}_3\text{H}_5^+\) have been studied experimentally only in vacuum by mass-selected IR spectroscopy [11–13]. Their stable isomers have been identified and IR spectra interpreted. Numerous attempts have been made to study the allyl cation, \(\text{C}_3\text{H}_5^+\), by NMR spectroscopy in liquid superacids at low temperature, and they have failed [14]. The formation of \(\text{C}_3\text{H}_5^+\) has been proved in a cryogenic superacidic matrix (170 K) by IR spectroscopy [15,16]. With the increasing temperature (230 K), the IR spectrum changes and this phenomenon is attributed to ”polymerization”. The main disadvantages of the conventional use of superacids such as \(\text{FSO}_3\text{H}/\text{SbF}_5\) are the high oxidation potential and reactivity of the Lewis acid used, \(\text{SbF}_5\), which lead in the case of vinyl cations to rearrangement or decomposition products at temperatures above ~100 °C [17,18]. Nevertheless, NMR spectroscopy has revealed the formation (in liquid superacids) of unstabilized \(\text{C}_5^\text{dienyl cations}\) with two conjugated \(\equiv\text{C}\) bonds at ~135 °C [18] and more stable cyclobutenyl and dimethyl-allyl cations [19–21]. The vinyl cations stabilized by β-silyl and other electron-donating groups were studied in the 1990s by H.-U. Siehl and coauthors [22–24] by NMR spectroscopy in liquid superacids.
at temperatures below −100 °C and were isolated as carborane salts [25]. Thus, from refs. [15–25], it follows that nonstabilized vinyl cations are stable only at low temperatures (less than −100 °C), and their salts are not isolable in a pure state. Recently, it was shown that this is not the case: carborane salts of the vinyl and allyl types of carbocations C₃H₅⁺ and C₄H₇⁺, stable at room and elevated temperatures (up to 140–150 °C), were obtained and characterized by X-ray diffraction analysis and IR spectroscopy [26–28]. The possibility of the existence of carbocations containing C≡C bonds is discussed on the basis of quantum chemical calculations [29], but they have not been obtained and characterized experimentally.

In this work, we report obtaining pure solid salts—stable at room temperature—of the unsaturated carbocations with double C=C (C₄H₅Cl⁺) and triple C≡C bonds (C₄H₇⁺) and a so far unknown divinyl chloronium cation, (C₂H₃)₂Cl⁺. As counterions, carborane anions CHB₁₁Hal₁₁⁻ were chosen, where Hal=F, Cl (hereafter abbreviated as {F⁻} and {Cl⁻}, Figure 1) because of their extreme stability and minimal basicity, which promotes the formation of stable salts with highly reactive cations [30]. The cations being studied were characterized by ¹H/¹³C NMR and IR spectroscopy.

![Figure 1. Icosahedral carborane anion CHB₁₁Hal₁₁⁻ (Hal=F, Cl).](image)

2. Results and Discussion

2.1. The Chloronium Cation

It is formed by a three-stage reaction (see the Experimental Section). The first two stages

\[ \text{H } [\text{Cl}_{11} ] + \text{C}_2\text{H}_4\text{Cl}_2 \rightarrow \text{C}_2\text{H}_4\text{Cl}^+ [\text{Cl}_{11}^- ] + \text{HCl} \]

and

\[ \text{C}_2\text{H}_4\text{Cl}^+ [\text{Cl}_{11}^- ] + \text{C}_2\text{H}_4\text{Cl}_2 \rightarrow (\text{C}_2\text{H}_4\text{Cl}^+-\text{C}_2\text{H}_4\text{Cl}) [\text{Cl}_{11}^- ] \]

are similar to those studied for reactions of H[Cl₁₁] with CH₂Cl₂ [31] or C₂H₃Cl [32] and should lead to the formation of the salt of the dichloroethylchloronium cation, C₂H₄ClCl⁻·C₂H₄Cl. It decomposes rapidly with the release of two HCl molecules to form mostly expected divinylchloronium (third stage):

\[ (\text{C}_2\text{H}_4\text{Cl}^+-\text{C}_2\text{H}_4\text{Cl}) [\text{Cl}_{11}^- ] \rightarrow (\text{C}_2\text{H}_3^+-\text{C}_2\text{H}_3) [\text{Cl}_{11}^- ] + 2\text{HCl}. \]

It will be shown below that in the IR spectra of the obtained salt, characteristic bands of chloronium group C-Cl⁺-C are observed at 628 and 594 cm⁻¹, thereby unambiguously proving the formation of the chloronium cation.

The optimized structure of the cis-isomer of divinylchloronium at the B3LYP/6-311G++(d,p) level of theory is shown in Scheme 1 (isomer I) with some geometrical parameters (the trans-isomer is almost the same in terms of energy). The presence of two double C=C bonds in cation I does not rule out that under certain conditions, intramolecular cyclization with the formation of isomer II may occur (Scheme 1). The optimization of structure II shows that the C=C distance in the chloronium C-Cl⁺-C group decreases so much that the C=C bond and the four-membered carbon cycle can form (isomer III).
Thus, to nevertheless, Energetically, cations II and III are more favorable than I by 31.2 and 11.3 kcal/mol, respectively.

NMR spectra. The magic-angle spinning (MAS) $^{13}$C NMR spectrum of the isotope-substituted $^{13}$C-(C$_2$H$_3$)$_2$Cl$^+\{\text{Cl}_{11}^-\}$ salt (99 atom% $^{13}$C) with high-power $^1$H decoupling contains four signals (Figure 2). Although the integration of $^{13}$C NMR signals is not recommended, we will point out that in this spectrum, the intensities of the signals at (83.2 + 78.6), 60.6 and 43.9 ppm correlate as 2.0:0.95:1.0, respectively. The MAS NMR $^{13}$C spectrum registered without $^1$H decoupling shows that two signals at 83.2 and 78.6 ppm are split with a $^1$H constant of 304 Hz (Figure 2, red), which indicates that they belong to the C atoms of nonequivalent C$_a$H groups (Scheme 1). The other two signals obviously belong to carbon atoms of nonequivalent C$_b$H$_2$ groups. They must have a triplet structure. Nevertheless, due to the weaker influence of the positive charge on them, the spin–spin $^{13}$C–$^1$H constant decreases, thereby leading to signal broadening without multiplet resolution. Thus, the chloronium cation contains two nonequivalent CH$_2$CH groups.

![Scheme 1. The optimized structures of isomers of chloronium cation C$_4$H$_8$Cl$^+$.](image1)

![Figure 2. The $^{13}$C MAS NMR spectrum of the isotope-substituted $^{13}$C-(C$_2$H$_3$)$_2$Cl$^+\{\text{Cl}_{11}^-\}$ salt (99% $^{13}$C) with (black) and without (red) high-power $^1$H decoupling. Signals of the one vinyl group differing from another are marked with asterisks.](image2)

The $^1$H MAS NMR spectrum of the (C$_2$H$_3$)$_2$Cl$^+\{\text{Cl}_{11}^-\}$ salt (with the natural abundance of the $^{13}$C isotope) shows the known signal from the CH group of the [Cl$_{11}^-$] anion at 3.37 ppm and overlapped signals from the cation (Figure 3). In the $^1$H MAS NMR spectrum of the isotope-substituted $^{13}$C-(C$_2$H$_3$)$_2$Cl$^+\{\text{Cl}_{11}^-\}$ salt, signals from the cation are broadened due to spin–spin $^1$H–$^{13}$C coupling without fine structure resolution. To obtain a high-resolution spectrum, the $^{12}$C-(C$_2$H$_3$)$_2$Cl$^+\{\text{Cl}_{11}^-\}$ salt was dissolved in SO$_2$ClF and a $^1$H NMR spectrum was registered. It turned out to be-time dependent: the HCl signal appears at 1.06 ppm and its intensity increases until the intensity of the CH signal of the
[Cl$_{11}^-$] anion is reached. This means that chloronium in solution decomposes with the release of one HCl molecule:

$$(\text{C}_2\text{H}_3)_2\text{Cl}^+\{\text{Cl}_{11}^-\} \rightarrow \text{C}_4\text{H}_5^+\{\text{Cl}_{11}^-\} + \text{HCl}. $$

![Figure 3. $^1$H MAS NMR spectrum of the (C$_2$H$_3$)$_2$Cl$^+$[Cl$_{11}^-$] salt.](image)

The $^1$H NMR spectrum of the freshly prepared solution (recorded within 2–3 min after solution preparation at room temperature) shows strong signals from the chloronium cation and weak signals from HCl and the products of decomposition (Figure 4). Because a solid suspension in a liquid does not have time to completely precipitate within 2–3 min, the resolution of the spectrum is low and the $^3J_{HH}$ decoupling is not observed. The spectrum shows all six signals expected for that of the asymmetric cation (C$_2$H$_3$)$_2$Cl$^+$. They correlate with the signals in the $^1$H MAS NMR spectrum subjected to separation into six Lorentzian components (Figure 3). Therefore, the $^1$H NMR spectra of chloronium are similar for a solution and the solid salt, and cation structure is the same in both phases.

The finding that each C$_2$H$_3$ group of the (C$_2$H$_3$)$_2$Cl$^+$ cation yields three H$^1$ signals (H$_a$, H$_b$, and H$_c$) that are known for neutral vinyl chloride with hindered rotation of the CH$_2$ group around the C=C bond [33] means that C$_2$H$_3$ groups contain a double bond. That is, the cation under study is distorted divinylchloronium with two nonequivalent C$_2$H$_3$ groups. Its asymmetry in solid salt (C$_2$H$_3$)$_2$Cl$^+\{\text{Cl}_{11}^-\}$ and in solutions may be due to the emergence of contact ion pairs with cation–anion interaction via the C$_\alpha$H group (Scheme 2). In neutral vinyl chloride, the C$_\alpha$ atom of CH$_2$C$_\alpha$Cl is mostly deshielded because it is mainly affected by the electronegativity of the Cl atom, while atoms of the CH$_2$ group are deshielded less [33,34] (Table 1). The same is observed in cation I: the C$_\alpha$ atom closest to Cl$^+$ is more deshielded than the C$_\beta$ atom. There is also an important difference: the screening of H and C atoms in the chloronium cation is greater than that of vinyl chloride, i.e., the charge of the cation contributes to an increase in the screening constant of the C and H atoms.


Scheme 2. Schematic representation of the structure of cation I with magnetically nonequivalent H atoms a and b involved in ion pairing with an anion.

Figure 4. The $^1$H NMR spectrum of the (C$_2$H$_3$)$_2$Cl$^+$[Cl$_{11}^-$] salt dissolved in SO$_2$ClF. The signals from the vinyl group that more strongly bonded with the Cl$^+$ atom are labeled with an asterisk. The signals from the decomposition products that grow with time are marked with the “♣” sign. Designations $H_a$, $H_b$ and $H_c$ are given in the Scheme 2.

Table 1. $^1$H/$^{13}$C NMR chemical shifts (ppm) of the chloronium cation in the (C$_2$H$_3$)$_2$Cl$^+$[Cl$_{11}^-$] salt in comparison with those of vinyl chloride (the signals marked with an asterisk belong to the second C$_2$H$_3$ group, which differs from the first one).

| Atom | Cation I Solid | Cation I Solution | CH$_2$CHCl $^{[33,34]}$ | Atom | Cation I Solid | CH$_2$CHCl $^{[33,34]}$ |
|------|----------------|------------------|------------------------|------|----------------|------------------------|
| $H_a$ | 5.58 | 4.87 | 6.13 | C$_\alpha$ | 83.2 | 78.6 * | 124.9 |
|     | 5.14 * | 4.49 * |           |                  |      |             |                        |
| $H_b$ | 4.77 | 4.11 | 5.23 | C$_\beta$ | 60.6 | 43.9 * | 116 |
|     | 3.97 * | 3.49 * |           |                  |      |             |                        |
| $H_c$ | 2.73 | 2.91 | 5.39 |           |      |             |                        |
|     | 2.22 * | 2.49 * |           |                  |      |             |                        |

IR spectra. In Figure 5, IR spectra of the salts of protio and deuterio chloronium cation are given. To identify the frequencies of CH, CC, and CCl vibrations, the difference in the spectra between the protio and deuterio samples was obtained with such a scaling factor as to fully compensate for the adsorption of the [Cl$_{11}^-$] anion. This difference allowed us to determine the bands of the protio cation with positive intensities and those of the deuterio cation as negative in the entire frequency range. The frequencies involving the C−H (D) vibrations yielded a common H/D isotopic ratio of 1.326 to 1.367 (Table 2). For the split band at 1238 cm$^{-1}$, this ratio is 1.024, confirming its assignment to the CC stretch. Two C−Cl stretches of the bridged C−Cl$^+−$C group at 628 and 594 cm$^{-1}$ (very specific for chloronium
cations [31,32]) remained nearly the same, as did another one at 740 cm$^{-1}$, confirming that it did not involve vibrations from the H atom (can be a CICC bending vibration).

The IR spectrum of the chloronium cation has two specific features. The first and most important is the absence of a strong C=C stretching band expected at ~1600 cm$^{-1}$. Instead, it shows a split band of medium intensity at 1238 and 1234 cm$^{-1}$, which is even lower than that of the t-Bu$^+$ cation (~1290 cm$^{-1}$). If this is indeed the band of the CC stretch vibration of cation I, then it is slightly stronger than the strengthened single C-C bond in the t-Bu$^+$ cation, but weaker than the aromatic CC bond with one-and-half-bond status.

The second feature is the multiplet structure of the bands of CH$_2$/CD$_2$ stretch vibrations (Figure 5, Table 2); this arrangement is caused by the nonequivalence of the two C$_2$H$_3$ groups of cation I owing to ion pairing. In the salts with carborane anion \{F$_{11}^-$\}, which is much less basic than [Cl$_{11}^-$], the ion pairing should weaken or not form at all. The IR spectrum of the C$_4$H$_6$Cl$^+\{F$_{11}^-$\} salt contains three CH stretch vibrations of the cation (Figure 6). Their frequencies are strictly proportional to the frequencies of vinyl chloride [35]: $\nu_{as}$CH$_2$ 3121 cm$^{-1}$, $\nu_s$CH$_2$ 3030 cm$^{-1}$ and $\nu$CH 3086 cm$^{-1}$. These data allow their assignment (Figure 6) corresponding to symmetrical cation I. That is, the chloronium cation is uniformly surrounded by [F$_{11}^-$] anions. In the region of expected C=C stretching frequencies, a very weak band at 1607 cm$^{-1}$ is observed. Nevertheless, when the salt is heated to 100 °C and chloronium is completely decomposed with the release of HCl (see

![Figure 5. IR spectra in transmittance of the (C$_2$H$_3$-Cl$^+$-C$_2$H$_3$) [Cl$_{11}^-$] salt (red) and its deuterated analog (blue). Asterisks indicate bands of the [Cl$_{11}^-$] anion (two bands of CH stretching of the anion of variable intensity are observed due to the partial involvement of the CH group in H bonding). For a better examination of the bands of CH stretching vibrations, the difference between the protio and deuto spectra is shown (dashed black curve). The intensities of both spectra are reduced to unit anion intensity. Table 2. Comparison of the IR spectra of cations C$_4$H$_6$Cl$^+$ and C$_4$D$_6$Cl$^+$ in their salts with the [Cl$_{11}^-$] anion.](image-url)

| Sample | C-H Stretches | C-H Bending | CC Stretch | CH Bending | CCCI Bending | CCI*C Stretches |
|--------|---------------|-------------|------------|------------|--------------|----------------|
| protio | 3055 3044     | 2987 2974 2961 2938 | 1418 * 1324 1269 | 1238 | 914 | 740 | 628 594 |
| deuterio | 2303 2295 | 2244 2218 2191 2171 | **   ** 960 | 1208 | 694 | 748 | 635 582 |
| ratio  | 1.327 1.326 | 1.331 1.341 1.351 1.353 | - - 1.323 | 1.024 | 1.320 | 0.989 | 0.989 1.020 |

* Average of three components; ** overlapped with the anion.

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Experimental section), a new intense $\nu_{C=C}$ band of the decomposition product emerges at 1567 cm$^{-1}$, and a weak band at 1607 cm$^{-1}$ remains unchanged (Figure 6). This result indicates that the latter band belongs to one of the formed by-products. Thus, the symmetric chloronium cation, just as the asymmetric one, does not show the absorption of the stretching vibration of the C=C double bond in the expected frequency range.

![Absorbance spectra](image)

**Figure 6.** The ATR IR spectrum of the (C$_2$H$_2$-Cl$^+$-C$_2$H$_3$) [F$_{11}^-$] salt (red) and the same reduced by a factor of 5 along the vertical axis to show the absorption of C-F vibrations of the anion (dashed curve). The spectrum of the salt after heating at 100 °C for the C=C stretch region is highlighted in blue. Asterisks denote bands of the [F$_{11}^-$] anion.

A comparison of the experimental spectrum of chloronium with those calculated for optimized structures of isomers I–III at the B3LYP/6-311G++(d,p) level of theory (Table S3 in SI) does not show good agreement (especially for C=C stretch frequencies), which is generally typical for unsaturated carbocations [26,27].

Nevertheless, it is useful to compare the experimental stretch vibrations of the C–Cl$^+$–C group, which are the most specific indicators of chloronium cations, with those calculated for I–III isomers, given that the $\nu_{\text{calc}} / \nu_{\text{exp}}$ ratio must be close to 1.0. For isomer I, empirical frequencies are closest to calculated ones with the $\nu_{\text{calc}} / \nu_{\text{exp}}$ ratio of 0.91 (Table 3). For isomers II and III, this ratio is unsatisfactorily low, which is a sufficient reason to exclude them from consideration.

**Table 3.** A comparison of the stretch vibrations of the C–Cl$^+$–C group of the chloronium cation under study with those calculated for isomers I–III at the B3LYP/6-311G++(d,p) level of theory.

| Isomer  | Stretch Vibrations of C-Cl$^+$-C Group, cm$^{-1}$ |
|---------|-------------------------------------------|
|         | (calc / exp)                               |
| C$_2$H$_2$Cl$^+$ (exp) | 628                                        |
| I (calc)  | 568 (0.91)                                 |
| II (calc) | 494 (0.79)                                 |
| III (calc)| 478 (0.76)                                 |

*without scaling.
2.2. The C₄⁺-Carbocations

Salts of the chloronium cation decompose at temperatures above 100 °C with the release of HCl and the formation of carbocation C₄H₅⁺ (see the Experimental part). Three noncyclic isomers—IV, V, and VI—with the lowest energy are possible (the energy of V and VI exceeds that of IV by 5.8 and 8.00 kcal/mol, respectively) [29]. Their optimized structures at the B3LYP/6-311G++(d,p) level of theory are depicted in Scheme 3 with CC distances. Let us consider with which isomer the NMR and IR spectra of the C₄H₅⁺ cation are the most consistent.

![Scheme 3. Optimized structures of lowest-in-energy open-chain isomers of the C₄H₅⁺ cation.](image)

**NMR spectra.** The ¹H MAS NMR spectrum of the isotope-substituted ¹³C-C₄H₅⁺[Cl₁₁⁻] salt is given in Figure 7. It features a signal from the (¹³C)-H atom of the anion at 3.37 ppm and three signals from the cation. The intensity of the strongest signal at 2.55 ppm exceeds that of the anion by 3.3-fold, indicating that it belongs to the CH₃ group of the cation. Two other signals of equal intensity at 7.44 and 9.35 ppm obviously belong to two CH groups of the cation. This result clearly supports the formation of isomer VI. The signal at 7.44 ppm is a doublet with a ¹JC₄H coupling constant of 184 Hz. Other cation signals should also be unresolved doublets because all H atoms are bonded to one ¹³C atom.

![Figure 7. The ¹H MAS NMR spectrum of the C₄H₅⁺[Cl₁₁⁻] salt. The components of each split signal are shown in one color.](image)

The ¹H NMR spectrum was separated into Lorentzian components, taking into account the fact that the cation signals are doublets, and the anion signal is a singlet (Figure 7). A well-resolved doublet at 7.44 ppm may belong to the H atom of the H-(C≡C) group, and
the signal at 9.35 ppm should be attributed to the H atom of the CH[CH₃] group, because the broadening of the doublet components due to the spin–spin interaction with hydrogen atoms of the methyl group impairs their resolution.

13C MAS NMR analysis with high-power 1H decoupling yields four signals of this sample (Figure 8). The 13C NMR spectrum registered without 1H decoupling does not result in the manifestation of a fine structure owing to 13C-1H spin–spin interactions. The signal with a chemical shift of 36 ppm is typical for the CH₂ group in carbocations. To interpret the remaining signals, it is desirable to see their hyperfine structure. For this, it is necessary to record the NMR spectra of salt solutions, if possible.

![Figure 8. 13C MAS NMR analysis with high-power 1H decoupling of the 13C-C₄H₅⁺ {Cl₁₁⁻} salt. Each signal and the corresponding spinning sidebands, marked with asterisk, have the same color.](image)

The salt of cation VI was dissolved in SO₂ClF. Gaseous SO₂ClF was liquefied in an NMR tube at −15 °C using a stream of gaseous SO₂ClF passed through a desiccant P₂O₅. The 1H NMR spectrum of the solvent showed a weak broad signal at 8.90 ppm from H⁺(H₂O)_n, and a second one at 1.06 ppm from molecular HCl, which is formed upon the decomposition of SO₂ClF with water. That is, the solvent contained HCl and H⁺(H₂O)_nCl⁻ as impurities. The solution was obtained by the anaerobic condensation of SO₂ClF in an NMR tube with the 13C-C₄H₅⁺{Cl₁₁⁻} salt at the bottom; the tube was sealed and shaken until a saturated solution was obtained. Its 1H NMR spectrum contained weak solute signals along with a weak H⁺(H₂O)_n signal that broadened and shifted to 7.1 ppm, indicating a decrease in water protonation. At the same time, the HCl signal almost disappeared. All of these data mean that HCl joined the cation.

The 1H NMR spectrum of the solute shows a known singlet from the CH group of the anion (3.37 ppm) and four signals from the cation, which are split into doublets due to the 1H–13C spin–spin interaction (Figure 9). The integrals of the cation signals strictly conform to the 1:1:1:3 ratio. Thus, this carbocation is not the same as that in the original solid salt. It has one CH₃ group (at 2.69 ppm) and three CH groups. Obviously, upon salt dissolution, the HCl molecule joins the formal triple CC bond of cation VI to form the C₄H₆Cl⁺ cation VII (Scheme 4).

![Scheme 4. The joining of HCl to the cation (VI) with the formation of cation (VII).](image)
Figure 9. The $^1$H NMR spectrum of the C$_4$H$_6$Cl$^+$[Cl$_{11}^-$] solution in SO$_2$CIF. The broad signal at ~7 ppm belongs to protonated water.

In the $^1$H NMR spectrum of cation VII, the signal of the CH$_3$ group at 2.69 ppm is a doublet with $^1$J$_{H-C}$ = 130 Hz. Each doublet component is split into a quartet because of a spin–spin interaction of $^1$H with nucleus H$_{\alpha}$, C$_{\alpha}$ and C$_{\beta}$ with $^2$J$_{H-C_\alpha}$ ≈ $^3$J$_{H-C_\alpha}$ ≈ $^3$J$_{H-C_B}$ ≈ 7 Hz. Two other signals at 7.04 ppm and 8.42 ppm with constants $^1$J$_{H-C}$ = 168 and 158 Hz, respectively, are characteristic of the CH groups with sp$^2$ hybridization of the carbon atom and belong to the middle groups, C$_{\alpha}$H and C$_{\beta}$H. The doublet at 8.42 ppm has a quintet-like structure due to the spin–spin interaction of the H$_{\alpha}$ atom with the protons of the CH$_3$ and CH$_{\beta}$ groups and the C(H$_3$), C$_{\beta}$ and C$_{\gamma}$ carbon atoms. If all of the constants of these interactions are approximately the same and equal to 7 Hz, then the splitting will be quintet. The doublet signal at 7.04 ppm with $^1$J$_{H-C}$ = 168 Hz belongs to the H$_{\beta}$ atom. Its multiplicity is poorly resolved due to the spin–spin interaction of the H$_{\beta}$ atom with more differentiated atoms of groups C$_{\alpha}$H and C$_{\gamma}$H. Finally, the signal at 9.58 ppm with $^1$J$_{CH}$ 183 Hz does not have ultrafine structure and belongs to the terminal C$_{\gamma}$H(Cl) group. Its increased $^1$J$_{C-VH}$ compared to $^1$J$_{C_{\beta}H}$ (168 Hz) can be explained by the high electronegativity of the Cl atom bound to C$_{\gamma}$.

The $^{13}$C NMR spectrum of the same solution recorded with broad-band decoupling $^{13}$C $^1$H shows four signals (Figure 10, black). The signal at 20.8 ppm is a doublet with $^1$J$_{CC}$ = 39 Hz. It belongs to the sp$^3$ C atom of the methyl group interacting with the C$_{\alpha}$ atom’s spin with sp$^2$ hybridization. The components of this doublet are also split into doublets owing to a long-range interaction with C$_{\beta}$, with $^2$J$_{CC_\beta}$ = 7 Hz. The signal at 129 ppm is a triplet belonging to the C$_{\beta}$ atom bound to C$_{\alpha}$ and C$_{\gamma}$ atoms with $^1$J$_{CC}$ = 60 Hz, typical of the $^3$C$_{sp^2}$-$^3$C$_{sp^2}$ constants. The signal at 186 ppm is a superposition of two doublets with $^1$J$_{C-C}$ = 60 Hz. It belongs to the C$_{\alpha}$ atom bound to significantly different atoms, C(H$_3$) and C$_{\beta}$. Finally, the doublet signal at 203 ppm with the constant $^1$J$_{CC}$ = 60 Hz belongs to the C$_{\gamma}$ atom of the C$_{\gamma}$HCl terminal group.

The monoresonance $^{13}$C NMR spectrum of this solution is in agreement with the signal assignment proposed above (Figure 10, blue). The signal of the CH$_3$ group is split into a triplet with $^1$J$_{C-H}$ = 130 Hz ($^1$J$_{C-C}$ = 39 Hz); the C$_{\beta}$ signal is split into two triplets with $^1$J$_{C-H}$ = 168 Hz ($^1$J$_{C-C}$ = 60 Hz); two doublet C$_{\alpha}$ signals are doubled with $^1$J$_{C-H}$ = 158 Hz ($^1$J$_{C-C}$ = 60 and 39 Hz) and the signal from the C$_{\gamma}$ atom shows a split doublet with $^1$J$_{C-H}$ = 183 Hz and $^1$J$_{C-C}$ = 60 Hz. All data from the $^{13}$C NMR spectrum of cation VII are summarized in Table 4.
In the 1H NMR spectrum of cation VII, the CH3 group (at 2.69 ppm) and three CH groups are resolved due to the spin–spin interaction of the Hβ and C atoms. Obviously, upon salt dissolution, the HCl molecule joins the formal triple CC bond of cation VI, forming the HCl signal almost disappeared. All signals from the cation, which are split into doublets due to the spin–spin interaction of 1H with nucleus Hα and C168 Hz, belong to protonated water.

To test whether there was a similarity between the chemical shifts of the 13C signals of cation VII and VI, the interpreted signals from VII were compared with those from VI. An unexpectedly good correlation was obtained (Figure 11), which implies that the shielding of 13C nuclei in carbon skeletons $\text{C}_\gamma \text{C}_\beta \text{C}_\alpha \text{C}_(\text{H}_3)$ of both cations was similar. Based on this similarity, it is possible to interpret the 13C signals of cation VI (Table 5).

**Table 4.** NMR data $^a$ for cation VII in a SO2ClF solution.

| Nucleus  | CH3 | CαH | CβH | CγH (Cl) |
|----------|-----|-----|-----|---------|
| $^1$H δ | 2.69| 8.42| 7.04| 9.58    |
| $^1$JCH | 130 | 158 | 168 | 183     |
| $^2$JHH | 7   | $^b$| 7   | $^b$    |
| $^13$C δ| 20.8| 183.6| 129.2| 203.6   |
| $^1$JCC | 39  | 60  | 60  | 60      |

$^a$ Chemical shifts are in parts per million, coupling constants are in hertz. $^b$ not determined.

**Table 5.** Chemical shifts $\delta^*$ in the MAS NMR spectra of isomer VI in its C4H5$^+\{\text{Cl}_{11}^−\}$ salt.

| Nucleus  | CH3 | CαH | Cβ | CγH ($^1$JCH in Hz) |
|----------|-----|-----|----|---------------------|
| $^1$H    | 2.25| 9.35| -  | 7.44 (184)          |
| $^13$C   | 36  | 215 | 150| 231                 |

$^*$ in ppm, for $^1$H vs. internal standard, the H(C) signal of the anion, equal to 3.37 ppm in a dichloromethane solution.
products are formed, they are unstable and quickly transform into the final product. It is similar to
the deutero isomer (Scheme 5). Therefore, if isomer IV comes into being at the first stage, then it quickly transitions into isomer VI (Scheme 5).

IR spectra. The formation of the C₄H₅⁺ cation from chloronium at 120 °C results in the disappearance of the bands of the most characteristic stretch vibrations of the C-Cl⁻-C moiety of chloronium, and in the appearance of a new spectrum with a highly intense band at 1563 cm⁻¹, typical of the stretching vibrations of the multiple CC bond of unsaturated hydrocarbons (Figure 12). The sequential recording of IR spectra with increasing temperature does not yield absorption bands of any intermediates, except for the spectrum of the final product, which increases in intensity. This means that if intermediate products are formed, they are unstable and quickly transform into the final product. It is expected that the decomposition of chloronium produces isomer IV, which, according to quantum chemical calculations, has the lowest energy among all the open-chain isomers, IV–VI [29]. Nevertheless, according to NMR spectra, cation VI is formed. Therefore, if isomer IV comes into being at the first stage, then it quickly transitions into isomer VI (Scheme 5).

Figure 11. Correlation between chemical shifts of interpreted signals of ¹³C NMR of the cation VII and those of the cation VI.

Figure 12. IR spectra in transmittance of the protium-(red) and deuterium-(blue) C₄H₅⁺ carboxcation in their salts with the [Cl₁₁⁻] anion in the frequency range of CH stretches (a) and below 1600 cm⁻¹ (b). The intensities of both spectra are reduced to unit anion intensity.
Scheme 5. Proposed formation of the C₄H₅⁺ cation from the chloronium cation.

Stronger heating of the C₄H₅⁺[Cl₁₁⁻] salt to 200 °C does not induce any changes in the IR spectrum of carboxation VI, indicating its thermal stability. The IR spectra of C₄H₅⁺ are similar between its salts with [F₁₁⁻] and [Cl₁₁⁻] anions (Table S4 in SI), which means that its structure is not affected by any change in the basicity of the anionic environment. Because the absorption pattern of the [F₁₁⁻] anion overlaps with a larger part of the C₄H₅⁺ spectrum, as compared to that of [Cl₁₁⁻], we discuss the spectrum of C₄H₅⁺[Cl₁₁⁻] salt.

In Figure 12, the IR spectra of salts C₄H₅⁺[Cl₁₁⁻] and C₄D₅⁺[Cl₁₁⁻] are depicted. Their difference, obtained via the complete compensation of the absorption of the [Cl₁₁⁻] anion, allows detecting all bands of the protio-cation with positive intensity and those of the deuterio-cation with negative intensity. Pairs of bands with the H/D isotopic ratio of 1.34–1.36 belong to CH vibrations (Table 6). For the intense band at 1563 cm⁻¹ and the middle one at 1447 cm⁻¹ (protio-sample), this ratio is ~1.036 and 1.057, respectively, which means that they belong to the stretching vibrations of CC bonds. Their frequencies approach the double and one-and-a-half bond status, respectively, and the formal structure of the cation VI is more correctly represented as shown in Scheme 6. On the other hand, the CC stretch frequencies of cation VI can be considered as asymmetric (1563 cm⁻¹) and symmetric (1447 cm⁻¹) CCC vibrations. Then, structure VI can be described as resonance between two structures VIa and VIb (Scheme 6).

Table 6. IR spectra of C₄H₅⁺ and C₄D₅⁺ cations (isomers VI) in their salts with the [Cl₁₁⁻] anion.

|       | C₄D₅⁺ | H/D Ratio | Assignment * |
|-------|-------|-----------|--------------|
| 3058  | 2284  | 1.339     | νCαH (CαD) and νCβH (CβD) |
| 3039  | 2251  | 1.350     | ναCH₃ (CD₃) |
| 2942  | 2129  | 1.381     | 2νCC overtone |
| 2891  | -     | -         | ναCH₃ (CD₃) |
| 2871  | 2077  | 1.380     | ναCH₃ (CD₃) |
| 2829  | 2055  | 1.377     | ναH/δH (CD) |
| 1563  | 1521  | 1.028     | νC≡C |
| 1447  | 1368  | 1.057     | νCC |
| 1327  | 997   | 1.341     | δCH (CD) |
| 1303  | 971   | 1.341     | δCH (CD) |
| 964   | 719   | 1.354     | δCH (CD) |

* ν is the stretching mode; δ is the deformation mode.

Scheme 6. The structure of carboxation (VI), represented by two resonance structures (VIa) and (VIb).

The IR spectrum of unsaturated cation VII was found to have low intensity because its salt was obtained in a small amount by the evaporation of the solvent from its solution in SO₂ClF. Nevertheless, the most important frequencies are detectable with high confidence (Figure S2 in SI). The IR spectrum of VII does not contain an intense band of C=C stretching above 1600 cm⁻¹, which is present in the other studied isomers of the C₄H₆Cl⁺ cation, VIII...
(at 1680 cm$^{-1}$) and IX (at 1710 cm$^{-1}$), with $\pi$-electron density concentrated mainly on the C=C bond [28] (Scheme 7). Instead, its IR spectrum shows two bands of CC stretches at 1440 and 1262 cm$^{-1}$, whose low frequencies are more consistent with symmetrical and asymmetrical vibrations, respectively, of allyl moiety $\mathrm{C} \equiv \mathrm{C} \equiv \mathrm{C}$. The frequency of the C-Cl stretch vibration is seen at 636 cm$^{-1}$ (Figure S2 in SI), which is much lower than that of isomers VIII (at 768 cm$^{-1}$) and IX (at 733 cm$^{-1}$) [28] and matches the frequency of asymmetric vibration of the bridged C=Cl$^+$–C group of the stablest dimethylchloronium cation, which decomposes at elevated temperature [32]. Therefore, the C-Cl bond is weak, and with an increase in temperature, cation VII can lose the HCl molecule.

![Scheme 7](image)

**Scheme 7.** The structure of two vinyl-type isomers of the C$_4$H$_6$Cl$^+$ cation.

### 2.3. Comparative Discussion of the IR and NMR Spectroscopic Data

#### 2.3.1. The Chloronium Cation

Even though, according to calculations, cyclic cation III is energetically more favorable than open-chain I by 31.2 kcal/mol, it is I that forms in the solid salt and exists in solutions. A specific feature of cation I is its asymmetry in salts with $[\mathrm{Cl}_{11}^-]$ anions, owing to the ion pairing with the anion. In SO$_2$ClF solutions, cation I retains its asymmetry due to the formation of contact ion pairs. In a salt with the least basic $[\mathrm{F}_{11}^-]$ anions, the IR spectrum of the cation corresponds to a symmetrical one, as predicted by quantum chemical calculations for a naked cation I in vacuum. Such a high sensitivity of the cation to the influence of the environment indicates its high polarizability.

The asymmetry of cation I in ion pairs arises due to its interaction with the anion, not through its Cl atom, but rather through the C$_\alpha$H group, as illustrated in Scheme 2. In other words, the positive charge is more substantial on the C$_\alpha$H group.

The asymmetry of the cation is manifested mostly in the vibrations of its CH stretches rather than in those of its CC stretches, which differ only by 5 cm$^{-1}$. A comparison of its IR spectrum with the interpreted spectrum of neutral vinyl chloride [35] (without C-Cl and CCCI vibrations) allows the assignment of its most characteristic frequencies (Table S6 in SI), and shows a good correlation for all frequencies with the exception of that for C=C stretching (Figure 13), which deviates downward from the correlation line by 340 cm$^{-1}$. The frequency of the C-Cl stretch vibration is seen at 636 cm$^{-1}$ (Figure S2 in SI), which is much lower than that of isomers VIII (at 768 cm$^{-1}$) and IX (at 733 cm$^{-1}$) [28] and matches the frequency of asymmetric vibration of the bridged C=Cl$^+$–C group of the stablest dimethylchloronium cation, which decomposes at elevated temperature [32]. Therefore, the C-Cl bond is weak, and with an increase in temperature, cation VII can lose the HCl molecule.

Cation I also possesses unusual features in NMR spectra: the impact of the positive charge on its C$_2$H$_3$ groups increases the screening constants of the C atoms while weakening the C=C bond, compared to those of neutral C$_2$H$_3$Cl. Thus, a positive charge reduces the $\pi$-electron density between carbon atoms, bringing its nature closer to a single $\sigma$-bond (the screening of C atoms increases).

A comparison of cation I with its saturated analog, diethylchloronium (C$_2$H$_5$)$_2$Cl$^+$ [32], suggests that frequencies of symmetric and asymmetric stretching vibrations of the chloronium C-Cl$^+$–C group in I are higher by 80 and 83 cm$^{-1}$, respectively. This is a large difference. It means that the C-Cl$^+$–C group attracts electron density from the C$_2$H$_5$- group, thereby imparting a weak $\pi$-character to C-Cl bonds and reducing the $\pi$-character of the...
C=C bond. Thus, the C2H3 group under the influence of a positive charge becomes an
effective electron donor, attracting a positive charge.

Figure 13. Correlation between the empirical frequencies of the C2H3 group of the C2H3Cl molecule
and those of the (C2H3)2Cl+ cation.

2.3.2. The C4-Carbocations

When chloronium decomposes at >120 °C, the most stable isomer, IV, forms first
(Scheme 5). Nonetheless, if this happens, then IV quickly converts to VI, which, according
to quantum chemical calculations at the B3LYP/6-311G++(d,p) or MP2(full)/6-311G(d,p)
levels of theory, is energetically less favorable by 8.0 or 7.6 kcal/mol [29], respectively.
The calculations also predict that the transition of IV to VI takes place in two stages,
with an activation energy of 39 kcal/mol [29], which should prevent the formation of VI.
Nevertheless, the formation of isomer VI was revealed to be the most preferable.

Isomer VI in carborane salts can be in a homogeneous and inhomogeneous (with
predominant interaction with one counterion) anionic environment. Both states, differing
in ν=C=C frequencies, have been found for vinyl-type carbocations [26–28]. On the other
hand, isomer VI in salts with [Cl11−] and with the least basic [F11−] anion shows similar
frequencies of C≡C stretching, pointing to its homogeneous anionic environment.

The IR spectrum of isomer VI has two features related to the vibration frequencies
of C≡C and C-H stretches. The first one is νC≡C at 1563 cm−1, which is 73 cm−1 higher than
that of the C=C double bond (1490 cm−1) of cations (CH3)2C=C−H or CH3C+≡CH [26,27],
and this is expected. Nonetheless, the calculated C≡C stretch (at B3LYP/6-311G++(d,p)
level of theory, with a scaling of 0.967) is 2020 cm−1, which significantly exceeds the experimen-
tal one by 450 cm−1. A similar discrepancy between the calculated and experimental
values of the C=C stretching frequencies equal to 362–246 cm−1 has been documented for
vinyl carbocations, CH3-CH=CH+ and CH3-C+=CH2, respectively [26,27].

The second feature of the IR spectra of VI is the reduced frequency of stretching vibra-
tions of its CH3 group by ~120 cm−1 relative to those of neutral alkanes. This is possible if
the CH3 group is involved in hyperconjugation with the partially empty 2px orbital of the
Cα atom. The decrease in frequency is not very large compared to that observed for t-butyl+ and
i-propyl+ alkane carbocations (~160 cm−1), which have a well-pronounced hyperconju-
gation effect [6]. This observation clearly indicates that in isomer VI, the triple C≡C bond is
partially delocalized (Scheme 6) with the predominant contribution of resonance structure
VIa, because a weak contribution of resonance structure VIB promotes the weak filling of
the 2px orbital of the Cα atom and the hyperconjugation effect is partially attenuated.

The calculated IR spectrum of isomer VI revealed that its CH3 group should not
be disturbed by hyperconjugation (Table S5 in SI). Similarly, the calculated frequency of
the CγH group at 3137 cm⁻¹ is typical for the H-C≡C group of neutral molecules and exceeds the empirical one (at 3058 cm⁻¹) by ~80 cm⁻¹. Therefore, the application of quantum chemical calculations to the interpretation of IR spectroscopic data should be carried out with great care. The same conclusion was drawn earlier in a study on vinyl-type carbocations [26,27].

The obtained NMR spectra allow us to discern some pattern in their changes for alkanes, alkenes, and unsaturated carbocations. A strongly deshielded 13C NMR signal (>150 ppm relative to TMS) can be confidently assigned to a positively charged carbon atom. The largest chemical shift has been documented for the central carbon atom of the tert-butyl cation at 335.2 ppm [36]. In unsaturated carbocations, the C=C double bond is often delocalized, forming allyl moiety 1. Chemical shifts of its C atoms usually vary depending on the substituents attached to it: from 170 to 190 ppm for C1,3, and 170–150 ppm for C2 atoms, respectively [37], thus pointing to greater charge localization on atoms C1 and C3. If the double bond is not delocalized, as for example, in the moiety of the 1-cyclopropylcyclopropyl-dene methyl cation, then the positive charge is located mainly on the C2 atom with a chemical shift of 234 ppm and less on atoms C1 (51.7 ppm) and C3 (21.2 ppm) [38]. In vinyl-type carbocations R′C≡CR′′ stabilized by electron-donating groups R′ and R′′, such as , the positive charge on the C=C bond is greatly reduced due to the combined influence of t-Bu and the two β-silyl substituents directly attached to it [39]. In the C13 NMR spectra, the signal from the Cα atom is observed in a weak field at 202.7 ppm and from the Cβ atom at 75.5 ppm, that is, the charge is mainly localized on the Cα atom.

Vinyl cation VII, formally studied by us, has a double C=C bond in the moiety, whose carbon atoms possess the chemical shifts Cγ (203 ppm), Cβ (129 ppm) and Cα (183 ppm). They do not match a triatomic moiety with one CC double bond but rather correspond to slightly asymmetric allyl moiety . Therefore, it is more correct to represent structure VII as shown in Scheme 8.

![Scheme 8](image)

Scheme 8. Structure of isomer VII according to NMR and IR spectroscopy.

Cation VI formally contains a triple CC bond. According to the IR spectra, it is delocalized to form the moiety (Scheme 6). The chemical shifts of its C atoms (230 (Cγ), 150 (Cβ) and 215 ppm (Cα)) are consistent with those of the part of vinyl cation VII (Figure 11). This means that electron density distributions—across the CC bonds of the two moieties, which differ in formal double and triple CC bonds—are of the same type, with a lower positive charge on the Cα atom than on atoms Cβ and Cγ. The observed participation of H atoms of the CH3 group in hyperconjugation with the partially empty 2pz orbital of the Cα atom indicates its sp² hybridization. That is, formally, the Cα atom must carry a considerable positive charge.
3. Methods and Materials

The carborane acids, \(\text{H(CHB}_{11}\text{Hal}_{11})\) with \(\text{Hal}=\text{F, Cl}\), were prepared as described previously [40,41]. They were purified by sublimation at 150–160 °C under pressure of \(10^{-5}\) Torr on cold Si windows in a specially designed IR cell. The formed thin translucent layer yielded an intense IR spectrum. If this film is slightly wetted with a drop of 1,2-dichloroethane (DCE) and is allowed to dry quickly, the following reaction proceeds with the release of HCl:

\[
\text{H[Hal}_{11}] + 2 \text{C}_2\text{H}_4\text{Cl}_2 \rightarrow (\text{C}_2\text{H}_5\text{Cl}^+\text{C}_2\text{H}_3)(\text{Hal}_{11}^-) + 3\text{HCl. } (1)
\]

The amount of the formed HCl was determined as follows: the weighed portion of H\(\text{Cl}^+\) was placed on the bottom of the IR cell and wetted with a drop of DCE. The quantity of released HCl was determined by measuring the intensity of its absorption at 2821 cm\(^{-1}\) with subsequent conversion to millimoles using a calibration curve. The determined molar ratio HCl/H\(\text{Cl}^+\) is equal to 3 (Table S1 and Figure S1 in SI). Chemical analysis of the content of C and H in the salts of chloronium confirmed its chemical composition (Table S2 in SI).

When \(d_4\)-DCE is used, reaction (1) proceeds with the formation of (\(\text{C}_2\text{D}_3\text{Cl}^+\text{C}_2\text{D}_3\))\(\text{Cl}_{11}^-\) and the release of both HCl and DCl (detected in IR spectra). Thus, reaction (1) proceeds via two steps:

\[
\text{H[Cl}_{11}] + \text{C}_2\text{D}_4\text{Cl}_2 \rightarrow \text{C}_2\text{D}_4\text{Cl[Cl}_{11}] + \text{HCl,}
\]

and

\[
\text{C}_2\text{D}_4\text{Cl[Cl}_{11}] + \text{C}_2\text{D}_4\text{Cl}_2 \rightarrow (\text{C}_2\text{D}_3\text{Cl}^+\text{C}_2\text{D}_3)(\text{Cl}_{11}^-) + 2 \text{DCl. } (2)
\]

After completion of reaction (1), the product film formed on the surface of the Si windows has a yellow color due to the presence of impurities. These are easily removed by washing the film with cold dichloromethane (DCM), because they are readily soluble, whereas the main product dissolves slowly. The remaining film turns white and its IR spectrum confirms the removal of a small amount of impurities.

At \(\geq100 \, ^\circ\text{C}\) the chloronium cation decomposes into an unsaturated carbocation with the release of HCl, in accordance with Equation (3)

\[
(\text{C}_2\text{H}_3\text{Cl}^+\text{C}_2\text{H}_3)(\text{Cl}_{11}^-) \rightarrow \text{C}_4\text{H}_5^+\text{Cl}_{11}^- + \text{HCl,}
\]

in a way similar to the mechanism of diethyl-chloronium decomposition into the \(t\)-Bu\(^+\) cation [32]. The thermal decomposition of deuterated divinyl-chloronium proceeds similarly, with the formation of the salt of the \(\text{C}_4\text{D}_5^+\) cation and the release of DCl.

The salts of \(^{13}\text{C}\)-substituted \((\text{C}_2\text{H}_3)^+\) and \(\text{C}_4\text{H}_5^+\) cations were obtained via reactions (1)–(3) using \(^{13}\text{C}\)-dichloroethane (99 atom\% \(^{13}\text{C}\)) from Sigma-Aldrich (Taufkirchen, Germany).

Solutions of carbocation salts in SO\(_2\)ClF for NMR measurements were prepared under anaerobic conditions. A solid salt was placed at the bottom of an NMR tube. Through a capillary, gaseous SO\(_2\)ClF was injected into it. At \(-15 \, ^\circ\text{C}\), it was condensed into a liquid. The tube was sealed and shaken until a saturated solution was obtained. \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of the solutions were recorded on a Bruker DRX 500 spectrometer (Heidelberg, Germany). Chemical shifts in the \(^1\text{H}\) NMR spectra were measured relative to an internal standard, the \((\text{C})\text{H}\) signal of the anion \(\text{CHB}_{11}\text{Cl}_{11}^-\), which is equal to 3.376 ppm in a CH\(_2\)Cl\(_2\) solution referenced to TMS. Chemical shifts in the \(^{13}\text{C}\) NMR spectra were referenced to TMS as an external standard.

The preparation of samples for magic-angle spinning (MAS) NMR measurements is described in detail in the Supporting Information (SI).

The MAS NMR measurements were performed on a Bruker Avance-400 NMR spectrometer, Germany, (9.4 T) equipped with a broad-band double resonance MAS NMR probe (4 mm rotor diameter). The samples in the sealed glass ampoules were tightly inserted into MAS rotors and spun at 5–9 kHz. \(^{13}\text{C}\) MAS NMR spectra were recorded at ambient temperature at the resonance frequency of 100.63 MHz. The length of the 90° pulse was
within the framework of the Gaussian’09 package [43].

is formed with considerable alignment of the CC bonds in the VII was stable in solutions of its salt in SO$_2$Cl$_2$, which made it possible to obtain its detailed NMR spectra with hyperfine structure.

In propargyl carbocation, the C=C double and triple CC bonds, which contribute to the distribution of electron density over CC bonds and to the dispersion of a positive charge over the molecule.

The composition of the divinyl-chloronium cation is determined by the conditions of its preparation, and the structure is unambiguously proven by MAS NMR and IR spectroscopy. Its formal double C=C bonds have a bond status of less than one-and-half with low $\pi$-electron density between C-C atoms. At the same time, the electronic shielding of its C atoms is substantial, which is unexpected. The charge of the cation is concentrated mainly on the C$_2$H$_3$ groups, and this process considerably lowers its symmetry. All these features of the chloronium cation are indicative of its high polarizability.

In the C$_4$H$_6$Cl$^+$ cation, the electron density distribution over CC bonds and the nature of the double C=C bond are very sensitive to the position of the Cl atom in the carbon chain, $\overset{\gamma}{C}$$\overset{\beta}{C}$$\overset{\alpha}{C}$($\overset{\gamma}{H_3}$). When the Cl atom is attached to the C$_\alpha$/C$_\beta$, atom, isomers $\overset{+}{H_2C\overset{\gamma}{C}C\overset{\beta}{C}H_3}$ and $\overset{+}{H_2C\overset{\gamma}{C}C\overset{\beta}{C}H_3}$ arise, with well-defined and close-to-equivalent C=C double bonds. If the Cl atom is attached to the C$_\gamma$ atom, then allyl-type isomer VII is formed with considerable alignment of the CC bonds in the $\overset{\gamma}{C}$$\overset{\beta}{C}$ moiety, with the charge dispersed over it. This phenomenon drives strong change in the CC stretch frequencies.

4. Conclusions

Pure salts of the divinyl-chloronium cation, (C$_2$H$_3$)$_2$Cl$^+$, methylated propargyl (VI), and C$_4$-allyl type VII carboxocations with extremely stable and weakly basic carborane anions, CHB$_{11}$Cl$_{11}^-$ and CHB$_{11}$F$_{11}^-$, were obtained for the first time. They dissolved in DCM without interaction with the solvent but transformed into other carboxocations. Therefore, they were studied in a solid phase by IR and $^1$H/$^{13}$C MAS NMR spectroscopy. Only cation VII was stable in solutions of its salt in SO$_2$Cl$_2$, thereby refuting the widespread belief that unsaturated (nonaromatic) carboxocations are unstable at temperatures higher than $-100\,^\circ$C. The high stability of unsaturated carboxocations is facilitated by their formal double and triple CC bonds, which contribute to the distribution of electron density over CC bonds and to the dispersion of a positive charge over the molecule.

In the C$_4$H$_6$Cl$^+$ cation, the electron density distribution over CC bonds and the nature of the double C=C bond are very sensitive to the position of the Cl atom in the carbon chain, $\overset{\gamma}{C}$$\overset{\beta}{C}$$\overset{\alpha}{C}$($\overset{\gamma}{H_3}$). When the Cl atom is attached to the C$_\alpha$/C$_\beta$, atom, isomers $\overset{+}{H_2C\overset{\gamma}{C}C\overset{\beta}{C}H_3}$ and $\overset{+}{H_2C\overset{\gamma}{C}C\overset{\beta}{C}H_3}$ arise, with well-defined and close-to-equivalent C=C double bonds. If the Cl atom is attached to the C$_\gamma$ atom, then allyl-type isomer VII is formed with considerable alignment of the CC bonds in the $\overset{\gamma}{C}$$\overset{\beta}{C}$ moiety, with the charge dispersed over it. This phenomenon drives strong change in the CC stretch frequencies.
In propargyl carbocation VI, π-electron density of its formally triple C≡C bond is distributed to the neighboring C-C bond, thereby upgrading the neighboring bond to one-and-a-half-bond status and demoting itself to two-and-a-half-bond status. The asymmetry of the C≡C=CH₂ moiety is evidenced by the higher frequency of the νC≡C stretch at 1563 cm⁻¹ than that of the double C=C bond in vinyl cations (1490 cm⁻¹) [26,27]. Despite the asymmetry, the positive charge is effectively distributed over both CC bonds: the involvement of the hydrogen atoms of the CH₃ group in hyperconjugation with the 2pz orbital of the Cα atom means that it has sp² hybridization and a major positive charge is concentrated on it. Meanwhile, it follows from the MAS NMR spectra that a comparable charge is also localized on the Cᵥ atom.

Our important finding is that the charged formal triple C≡C bond in carbocation VI can accept an HCl molecule, giving rise to allyl cation VII with the Cl atom on a formal double C=C bond.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijms23169111/s1. References [35,44] are cited in the Supplementary Materials.

Author Contributions: Conceptualization, E.S.S.; methodology, E.S.S.; validation, E.S.S. and I.V.S.; formal analysis, I.V.S.; investigation, E.S.S. and I.V.S.; resources, I.V.S.; data curation, E.S.S. and I.V.S.; writing—original draft preparation, E.S.S. and I.V.S.; writing—review and editing, E.S.S.; visualization, E.S.S. and I.V.S.; supervision, E.S.S.; project administration, E.S.S.; funding acquisition, E.S.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of Science and Higher Education of the Russian Federation (state registration No. 1021052806375-6-1.4.3).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank Victor I. Mamatyuk for a useful discussion of the NMR spectra, Viktor Yu. Kovalskii for providing the quantum chemical calculations and Sergey S. Arsumanov for assistance with the recording of the MAS NMR spectra. The authors are grateful to the Multi-Access Research Center of the Siberian Branch of the Russian Academy of Sciences for spectral and analytical measurements.

Conflicts of Interest: The authors declare no conflict of interest.

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