Stabilization of carbocations CH$_3^+$, C$_2$H$_5^+$, i-C$_3$H$_7^+$, tert-Bu$^+$, and cyclo-pentyl$^+$ in solid phases: experimental data versus calculations†

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Comparison of experimental infrared (IR) spectra of the simplest carbocations (with the weakest carborane counterions in terms of basicity, CHB$_3$Hal$_2^-$, Hal = F, Cl) with their calculated IR spectra revealed that they are completely inconsistent, as previously reported for the tert-Bu$^+$ cation [Stoyanov E. S., et al. J. Phys. Chem. A, 2015, 119, 8619]. This means that the generally accepted explanation of hyperconjugative stabilization of the carbocations should be revised. According to the theory, one CH bond (denoted as CH*$_n$) from each CH$_n$/CH$_2$ group transfers its $\sigma$-electron density to the empty 2$p_z$ orbital of the sp$^2$ C atom, whereas the $\sigma$-electron density on the other CH bonds of the CH$_n$/CH$_2$ group slightly increases. From experimental IR spectra it follows that donation of the $\sigma$-electrons from the CH*$_n$ bond to the 2$p_z$ C-orbital is accompanied by equal withdrawal of the electron density from other CH bonds, that is, the electrons are supplied from each CH bond of the CH$_3$/CH$_2$ group. As a result, all CH stretches of the group are red shifted, and IR spectra show typical CH$_3$/CH$_2$ group vibrations. Experimental findings provided another clue to the electron distribution in the hydrocarbon cations and showed that the standard computational techniques do not allow researchers to explain a number of recently established features of the molecular state of hydrocarbon cations.

Most attention has been given to the tert-butyl cation, whose hyperconjugative delocalization of the positive charge has been used as a textbook explanation of its stability. As predicted by quantum chemical calculations, the most energetically stable tert-Bu$^+$ cation (C$_3$ symmetry) has three CH bonds, one from each CH$_2$ group, which are aligned in parallel with the empty 2$p_z$ orbital of the central sp$^2$ carbon atom.1,16–20 This situation makes donation of its $\sigma$-electron density to this orbital possible, resulting in $\sigma$-p$_z$ hyperconjugation (Scheme 1). These three C–H bonds (one of them is marked with • in Scheme 1) are weakened and their $\nu$CH frequencies are significantly decreased, whereas the remaining C–H bonds (CH’ and CH” in Scheme 1) are slightly strengthened and their $\nu$CH increases.

Thus, ab initio calculations predict a coherent picture of the mechanism underlying positive charge dispersion in the naked cations C$_2$H$_5^+$, (CH$_3$)$_2$CH$^+$ (i-Pr$^+$), and (CH$_3$)$_3$+$^+$ (t-Bu$^+$) primarily

Introduction

The research on carbocation stabilization is one of the most important trends in carbocation chemistry. Experimental studies mainly deal with gas phase infrared (IR) mass spectroscopy, IR and NMR characterization in superacidic media,$^5$–$^{12}$ and X-ray structural analysis.$^3$–$^4$ As shown by ab initio calculations, the isolated carbocations are stabilized due to the intramolecular charge distribution under the influence of hyperconjugation$^{1,18–22}$ and polarization.$^{23}$ The simplest carbocation, CH$_3^+$, is subject to only the polarization effect.$^{23}$ For the gaseous C$_2$H$_5^+$ cation, the theory predicts and experiments confirm that the hyperconjugative interaction between the CH$_2$ group and the empty 2$p_z$ orbital in the carbon atom of the CH$_2$ group is so strong that a bridged-proton symmetrical structure is formed. More attention has been given to the tert-butyl cation, whose hyperconjugative delocalization of the positive charge has been used as a textbook explanation of its stability. As predicted by quantum chemical calculations, the most energetically stable tert-Bu$^+$ cation (C$_3$ symmetry) has three CH bonds, one from each CH$_2$ group, which are aligned in parallel with the empty 2$p_z$ orbital of the central sp$^2$ carbon atom. This situation makes donation of its $\sigma$-electron density to this orbital possible, resulting in $\sigma$-p$_z$ hyperconjugation (Scheme 1). These three C–H bonds (one of them is marked with • in Scheme 1) are weakened and their $\nu$CH frequencies are significantly decreased, whereas the remaining C–H bonds (CH’ and CH” in Scheme 1) are slightly strengthened and their $\nu$CH increases.

Thus, ab initio calculations predict a coherent picture of the mechanism underlying positive charge dispersion in the naked cations C$_2$H$_5^+$, (CH$_3$)$_2$CH$^+$ (i-Pr$^+$), and (CH$_3$)$_3$+$^+$ (t-Bu$^+$) primarily

Scheme 1: Schematic representation of the electron density redistribution in accordance with the classical understanding of the mechanism of hyperconjugation stabilization in tert-Bu$^+$. 

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cp06839a
via the hyperconjugative effect. It is clear that the polarization effect must play an important role in cation stabilization although convincing data based on calculations are actually absent.

Our recent experimental study of the t-Bu\(^+\) cation in condensed phases, together with interpreted IR spectra of gaseous t-Bu\(^+\), showed\(^{28}\) that empirical findings contradict the generally accepted hyperconjugation mechanism (Scheme 1). It follows from the experiments that all C–H bonds of the two CH\(_3\) groups of t-Bu\(^+\) donate \(\sigma\)-electrons to the carbon’s 2p\(_\sigma\) orbital (Scheme 2), and the third CH\(_3\) group is mostly affected by polarization.

It should be noted that in condensed phases, there is an additional intermolecular effect of cation stabilization: hydrogen bonding with the immediate surroundings. It leads to the strengthening of hyperconjugation and contributes to the scattering of the positive charge to the environment.\(^{17,28}\)

In the present work we expanded the comparison of the computational results explaining stabilization of carbocations (structurally optimized and having the lowest energy) with empirical findings in IR spectra of carbocations in the series CH\(_3\)\(^+\), C\(_2\)H\(_4\)\(^+\), i-C\(_3\)H\(_7\)\(^+\), t-Bu\(^+\), and cyclo-C\(_6\)H\(_5\)\(^+\), with the carbaborane counterions (CHB\(_3\)Hal\(_{11}\), Hal = F, Cl; hereinafter abbreviated as {Hal\(_{11}\)}), see Fig. 1, whose conjugated acids are the strongest pure Brønsted superacids available today.\(^{24,30}\) We established that IR spectra of \{F\(_{11}\)\} or \{Cl\(_{11}\)\} in ionic carbocation salts are not dependent on the nature of the cation and therefore are not considered here. The aims of the present study were (i) to determine whether t-Bu\(^+\) is a special case of a cation or a common representative of saturated carbocations and (ii) to verify the compatibility of the theoretical data with experimental results for a range of simplest carbocations. We focused on the C–H stretch vibrations because they are mostly sensitive to hyperconjugation and polarization effects. Despite the importance of intermolecular hydrogen bonding for carbocation stabilization in the condensed phase, this effect will not be examined here in detail because it does not change the hyperconjugation mechanism when going from vacuum to a condensed phase as shown previously.\(^{17,28}\)

**Experimental**

All sample handling was carried out in an inert atmosphere (H\(_2\)O, O\(_2\) < 1 ppm) in a dry box. Carbaborane acids H{Hal\(_{11}\)} and their CH\(_3\){Hal\(_{11}\)} salts were prepared as previously described.\(^{30–33}\)

The salts of C\(_2\)H\(_3\)\(^+\) and C\(_3\)H\(_7\)\(^+\) cations with the \{F\(_{11}\)\} anion were obtained by reacting CH\(_2\)F with H{F\(_{11}\)} in an IR cell-reactor with simultaneous recording of the IR spectra of the formed cations.\(^{33}\)

The spectrum of the C\(_2\)H\(_3\)\(^+\){F\(_{11}\)} salt was also obtained in another way: instead of the H{F\(_{11}\)} acid, Et\(_3\)Si{F\(_{11}\)} was used, synthesized as described in ref. 30. A small drop of liquid 2-Cl-propane was added to an excess of solid Et\(_3\)Si{F\(_{11}\)} placed on the surface of the diamond attenuated total reflectance (ATR) accessory. A rapid reaction takes place

\[
\text{Et}_3\text{Si}\{\text{F}_{11}\} + \text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_5\text{F}\{\text{F}_{11}\} + \text{Et}_3\text{SiCl}^+, \tag{1}
\]

gaseous Et\(_3\)SiCl is quickly removed. An ATR spectrum of the formed solid revealed strong absorption of the i-C\(_3\)H\(_7\)\(^+\){F\(_{11}\)} salt and weak absorption of unreacted (excess) Et\(_3\)Si{F\(_{11}\)}. Computer subtraction of the weak spectrum of residual Et\(_3\)Si{F\(_{11}\)} allowed us to obtain a high quality spectrum of the i-C\(_3\)H\(_7\)^+{F\(_{11}\)} salt.

The cyclo-C\(_6\)H\(_5\)\(^+\){F\(_{11}\)} salt was obtained by means of direct interaction of liquid cyclo-pentane with a powder of H{F\(_{11}\)} in accordance with eqn (2):

\[
\text{cyclo-C}_6\text{H}_{10} + \text{H}\{\text{F}_{11}\} \rightarrow \text{C}_6\text{H}_5\text{F}\{\text{F}_{11}\} + \text{H}_2 \tag{2}
\]

It was reported\(^{30}\) that all alkanes, C\(_n\)H\(_m\) (\(n \geq 4\)), react with the H{F\(_{11}\)} acid in the same way. Reaction (2) proceeded under ambient conditions for 4 hours. A white powder of the C\(_2\)H\(_5\)\(^+\){F\(_{11}\)} salt was obtained from the solution after vacuum removal of the solvent, cyclo-pentane.

IR spectra of isopropyl and cyclo-pentyl carbocations with the \{Cl\(_{11}\)\} counterion were obtained as follows. A grain of the H{Cl\(_{11}\)} acid was placed on the top face of the diamond crystal of the attenuated total reflectance (ATR) accessory and was wetted with a small drop of liquid 2-chloropropane or chloro-cyclo-pentane; this amount was not sufficient for full acid utilization. This approach ensures stoppage of the reaction at the first-stage, as illustrated in eqn (3) (an example of preparation of the i-Pr\(^+\) salt):

\[
\text{C}_2\text{H}_5\text{Cl} + \text{H}\{\text{Cl}_{11}\} \rightarrow \text{C}_2\text{H}_5\text{F}\{\text{Cl}_{11}\}^- + \text{HCl}. \tag{3}
\]

Recording the spectrum without applied pressure allowed us to obtain the spectrum of the oily byproduct covering the diamond surface as a thin film. This byproduct is formed when an excess of the chlorine hydrocarbon interacts with an acid. Recording the spectrum of the solid particles crushed under pressure, which contained mainly the carbocation salt and an excess of unreacted acid, enabled us to obtain their spectra with a minor overlap with the spectrum of byproducts. Computer-based subtraction of the spectrum of the byproducts and excess acid allowed for isolation of the carbocation spectra.

IR spectra were recorded on a Perkin Elmer Spectrum-100 spectrometer in the 4000–400 cm\(^{-1}\) frequency range in transmission or ATR mode. The spectrometer was installed inside

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**Fig. 1** Icosahedral carbaborane anions of CHB\(_3\)Hal\(_{11}\) type (Hal = F, Cl) abbreviated as \{F\(_{11}\)\} or \{Cl\(_{11}\)\}. Halogen atoms are depicted in green.

**Scheme 2** Schematic representation of electron density redistribution in t-Bu\(^+\) according to empirical data.\(^{28}\)
the dry box. The spectra were manipulated using GRAMMS/A1 (7.00) software from Thermo Scientific.

Computational details
Geometric parameters of the species under study were optimized at the B3LYP-D3/def2-TZVPD level of theory\textsuperscript{44–37} using ultrafine grids. Equilibrium structures of compounds R{F\textsubscript{11}} and t-Bu{Cl\textsubscript{11}} were also calculated in a dichloroethane (DCE) solution ($\varepsilon = 10.125$) using the SMD solvation model.\textsuperscript{38} All stationary points were characterized as minima by a vibrational analysis (the number of imaginary frequencies [Nimag] was equal to zero), unless stated otherwise. Zero-point energies (ZPEs) were computed from the corresponding vibrational frequencies without scaling factors. (SMD-)B3LYP-D3/def2-TZVPD optimized structures were used in all subsequent computations.

To compare calculated and experimental vibrational frequencies, (SMD-)B3LYP-D3/def2-TZVPD harmonic frequencies were scaled by a factor of 0.9674 as recommended by Kesharwani et al.\textsuperscript{39} To obtain more accurate relative energies of some isomers, single-point high-level CCSD(T)/def2-TZVPD coupled-cluster computations\textsuperscript{35} within a frozen core approximation were additionally performed.

The energy decomposition analysis (EDA)\textsuperscript{41} was carried out for the most stable compounds at the B3LYP-D3/TZ2P level of theory using the scalar relativistic (SR) zeroth-order regular approximation (ZORA) Hamiltonian (core potentials were not used, and the quality of the Becke numerical integration grid was set to the keyword good).\textsuperscript{42}

SR-ZORA-B3LYP-D3/TZ2P computations were performed using the ADF2016 software,\textsuperscript{43–45} while the remaining gas-phase calculations in the gas phase and in a DCE solution were conducted using the Gaussian09 software.\textsuperscript{46} The natural bond orbital (NBO) analysis\textsuperscript{47,48} was performed for the species of interest as implemented in Gaussian09, def2-TZVPD basis sets were taken from the EMSL database.\textsuperscript{49,50}

Density functional theory (DFT) calculations with periodic boundary conditions were performed using the PBE functional\textsuperscript{51} with D3 dispersion correction\textsuperscript{56} using the VASP software package.\textsuperscript{52,53} The projector augmented wave (PAW) method\textsuperscript{54} was used to analyze the core states along with a plane-wave energy cutoff of 400 eV. Only the $I$ point was used for sampling the Brillouin zone.

The convergence criteria for electronic and structural optimization were set to $10^{-6}$ eV and $10^{-5}$ eV Å$^{-1}$, respectively. Harmonic vibrational frequencies were calculated by the finite difference method using the central difference with a step size of 0.015 Å.

All compounds were considered in their ground states. The spin-restricted formalism was employed for both DFT and CCSD(T) computations.

Results and discussion
Characterization of carbenocations on the basis of calculations
To obtain a unified computational view, we considered all carbenocations ($R'$) under study and their complexes with Ar and {F\textsubscript{11}}$^-$ in the gas phase and in solution at the same level of theory. The lowest-energy structures were chosen for subsequent analysis (see Fig. S1–S4 in ESI$^\dagger$ for a complete list of isomers). The results obtained for the $R'$, R'···Ar and R{F\textsubscript{11}} species are given in Tables S1–S5 in ESI$^\dagger$. The stretching vibrations and some valent angles for naked and solvated carbenocations are compared in Table 1.

The hyperconjugation effect is assumed to be the case starting from naked C\textsubscript{2}H\textsubscript{5}\textsuperscript{+}. In this cation, the hyperconjugation strength is so significant that the H\textsuperscript{+} proton is converted to the bridge state leading to a symmetrical structure (II.I in Fig. S1 in ESI$^\dagger$), which does exist in the condensed phase. Thus, we excluded the bridged structure from further analyses.

The C\textsubscript{2}H\textsubscript{5}\textsuperscript{+} structure becomes asymmetrical after solvation by the Ar atom via the C center. The CH\textsubscript{4}\textsuperscript{+} bond is oriented strictly parallel to the 2p\textsubscript{z} orbital of the sp\textsuperscript{2} C atom ($\theta = 0$, see Scheme 3) and the C—C—H\textsuperscript{+} angle is reduced (92.6°, Table 1); these data indicate a strong hyperconjugative interaction. The similar orientation of the CH\textsubscript{4}\textsuperscript{+} bond from each CH\textsubscript{3} group relative to the 2p\textsubscript{z} orbital of the sp\textsuperscript{2} C atom has only naked t-Bu\textsuperscript{+} (C\textsubscript{a}, $\theta = 2$°) and t-Bu···Ar solvate (C\textsubscript{b}, $\theta = 1$°). This finding corresponds to the generally accepted mechanism of carbenocation hyperconjugative stabilization (Scheme 1). Nevertheless, the $\theta$ angles of t-Bu\textsuperscript{+} (C\textsubscript{a}), despite almost the same relative energy as in t-Bu\textsuperscript{+} (C\textsubscript{b}), are increased by ca. 20°. The $\theta$ angle reaches values of 36° and 20° for the low-lying isomers of i-Pr\textsuperscript{+} (C\textsubscript{a}) and i-Pr····Ar (C\textsubscript{b}), respectively (Fig. S2 and S3 in ESI$^\dagger$), which means that one C—H bond from each CH\textsubscript{3} group is perpendicular to the vacant 2p\textsubscript{z} orbital, and two other C—H bonds are equivalently affected by hyperconjugation (Scheme 4). An intermediate case takes place in c-C\textsubscript{6}H\textsubscript{5}\textsuperscript{+} and c-C\textsubscript{6}H\textsubscript{5}···Ar species, with $\theta$ ranging from 12° to 13°. Thus, rotation of the CH\textsubscript{3} group by angle $\theta$ has a weak influence on the carbenocation hyperconjugation stabilization.

The strong hyperconjugation influence on the CH\textsubscript{3} group in asymmetric C\textsubscript{2}H\textsubscript{5}\textsuperscript{+}···Ar (Scheme 3) leads to a strong decrease in the CH\textsubscript{4}\textsuperscript{+} stretch to 2612 cm$^{-1}$, whereas frequencies of the other two CH\textsubscript{4}\textsuperscript{+} and CH\textsubscript{4}\textsuperscript{+} bonds (c-C\textsubscript{6}H\textsubscript{5}) are changed much less as compared to neutral hydrocarbons (Table 1). The $\nu$CH\textsubscript{2} and $\nu$CH\textsubscript{2} frequencies are highly characteristic and are not mixed (Fig. S5b in ESI$^\dagger$). Unlike C\textsubscript{2}H\textsubscript{5}\textsuperscript{+}, solvation of other carbenocations with Ar via the sp\textsuperscript{2} C atom has a slight effect on the calculated IR spectra (Table 1). The spectra of all carbenocations under study (both naked and solvated with Ar) show similar features: (i) the bands of C—H stretches affected by hyperconjugation are significantly red shifted and have increased intensity (only marked in Table 1); (ii) frequencies of the other C—H bonds of CH\textsubscript{3}/CH\textsubscript{2} groups are rather increased or are in the frequency region common for neutral hydrocarbons; (iii) the normal vibrations of these bonds or groups have a highly characteristic nature.

To gain insights into the bonding situation for the representative R'···Ar and R{F\textsubscript{11}} complexes, we performed the EDA (Table S1 in ESI$^\dagger$) and NBO analyses (Table S2 in ESI$^\dagger$). The results of our gas-phase calculations for the carbenocations paired with the {F\textsubscript{11}}$^-$ anion indicate the following: (a) in the case of R = C\textsubscript{2}H\textsubscript{5}, the hyperconjugation effect is the weakest one because of a covalent bond between ethyl and {F\textsubscript{11}}$^-$ leading to a modest energy gain corresponding to hyperconjugative stabilization ($\Delta E^{DH}_{ij} = 9.2$ kcal mol$^{-1}$; Table S2, ESI$^\dagger$) and rather weak IR intensity of
the corresponding CH stretch vibration (Table S4, ESI†); (b) the spectrum of i-Pr+ (Table S4 in ESI†) shows only some signs of weak hyperconjugation (two slightly decreased frequencies at 2923 and 2916 cm⁻¹ with somewhat increased intensity), suggesting that the bonding between i-Pr+ and {F₁₁} moieties is still covalent (ΔEorb) = 11.7 kcal mol⁻¹; Table S2, ESI†); (c) the spectra of cyclo-pentyl† and t-Bu† (Table S4 in ESI†) show greater resemblance to those of the corresponding Ar-solvated cations, as compared to the lighter carboxations.

NBO analysis revealed a polar covalent two-center two-electron C-F bond populated by 2.0 e at R = CH₃, C₂H₅, and i-Pr. Indeed, according to the EDA (Table S1 in ESI†), the electrostatic interaction (ΔEelstat, 52–79%) between R⁺ and {F₁₁⁻} moieties dominates over orbital (ΔEorb) and dispersion (ΔEdisp) interactions in all compounds. On the other hand, the energy of orbital interactions makes a noticeable contribution to the total attractive interactions when R = CH₃ (47%), C₂H₅ (42%), and i-Pr (34%), in line with the calculated IR spectra. Thus, a covalent contribution to the C-F bond is present in all cases and gradually decreases in the order R = CH₃ < C₂H₅ < i-Pr < cyclo-pentyl ≤ t-Bu simultaneously with the increase of hyperconjugative stabilization in the same order as can be seen from the corresponding ΔEelstat values (Table S2, ESI†).

However, as will be illustrated below, all solid R{F₁₁} compounds, except for CH₃{F₁₁}, are characterized by ionic bonding. The reason is the bulk effect, which most clearly manifests itself in the example of alkali halides. They are ionic in the solid state, but their neutral diatomics are linked covalently in the gas phase showing stretch vibration (for example, Na–Cl at 364.6 cm⁻¹). So, the crystal lattice promotes ionic binding.

To model the effect of the environment taking place in the condensed phase, we performed NBO and EDA analyses of the R{F₁₁} species when they are transferred from the gas phase to a DCE solution. This change of the phase is accompanied by an increase of the R–{F₁₁} distance (Tables S1 and S2, ESI†), which is relatively small for R = CH₃ (Δr = 0.03 Å) and pronounced when R = C₂H₅ (Δr = 0.12 Å), making the C-F bond more polar but retaining its covalent nature (ΔEelstat, 38–48%). In the case of i-Pr{F₁₁}, the lengthening of C-F is the most pronounced (Δr = 0.60 Å), indicating that the character of the bond changes to presumably ionic (ΔEelstat, 16%; ΔEelstat, 78%). Replacing i-PrH₂{F₁₁} with c-C₂H₅⁺ further increased the C-F separation to 2.58 Å, increasing the ionicity of the bond (ΔEelstat 12%). Finally, the c-C₂H₅⁺{F₁₁} compound has the C-F distance typical for ionic species (>2.6 Å, ΔEelstat, 11%; Table S4, ESI†). Similar results were obtained in SMD-B3LYP-D3/def2-TZVPD calculations for

### Table 1

| Compound | C₂H₅⁺ – Ar | i-Pr⁺ | i-Pr⁺ – Ar | t-Bu⁺ | t-Bu⁺ – Ar | c-C₂H₅⁺ | c-C₂H₅⁺ Ar |
|----------|------------|-------|------------|-------|------------|----------|------------|
| Symmetry | C₁         | C₂    | Cₛv        | C₁    | Cₛ        | C₁      | C₂        |
| NImag    | 0          | 0     | 1          | 0     | 1          | 0        | 0         |
| Relative energy, kcal mol⁻¹ | 0 | 0 | 0.2 | 0 | 0.1 | 0 | 0 |
| Dihedral angle, degrees | 0 | 17 | 36 | 13 | 20 | 21 | 2 |

*ΔE(CCD(T)/def2-TZVPD/B3LYP-D3/def2-TZVPD) + ZPE(B3LYP-D3/def2-TZVPD). The θ angle is shown in Scheme 3. Averaged values of angle θ are presented. The characteristic frequencies of C–H bonds mostly affected by hyperconjugation are boldfaced.
DCE solutions: the dielectric medium increased the separation between R and [Hal11] fragments (Fig. S4, ESI†), which made C–Hal bonds more ionic. The C–Cl distance in t-Bu[Cl11] became very close to that in an ionic salt (3.54 Å, Fig. S6, ESI†), resulting in a small covalent contribution—to the bonding between the ions (ΔEcoh 14%; Table S1, ESI†)—approaching that in the solid phase. The calculated CH stretch frequencies for both phases also correlate well (Table S5, ESI†).

Increasing the ionicity of the R[Fl11] compounds in the series R = C2H5 < i-Pr < cyclo-pentyl < t-Bu strengthens the effect of hyperconjugation, as followed from the corresponding ΔE[y] values (Table S2, ESI†) and from the increase in the red-shift and intensity of the bands of CH stretches involved in hyperconjugation (Table S4, ESI†). It should be noted that the condensed phase enhances both ionicity and the effect of hyperconjugation in this series of R[Fl11] compounds gradually; this result contradicts experimental findings.

We have proved previously26 that “effective” basicity of {Fl11−} in the solid salt, (HCO)[{Fl11−}], is close to the basicity of the Ar atom, and the calculated spectra of the Ar···H+–CO and CO–H+···Ar solvates agree well with the experimental spectra of ionic compound (CO)H+[Fl11−]. Therefore, the experimental IR spectra of the ionic bulk salts under study are expected to better match the calculated IR spectra of weakly bound R–Ar solvates rather than R−{Fl11−} species with a notable covalent contribution (Table S1 in ESI†). The same conclusion follows from DFT calculations for t-Bu[Cl11]: the structure of t-Bu+ in the t-Bu[Cl11] crystal (Fig. S7 in ESI†) is similar to that in the naked or Ar-solvated carbocation rather than to the structure of molecular compound t-Bu[Cl11] with a distorted t-Bu+ moiety (Fig. S6a in ESI†). To sum up, computational results obtained for R−Ar (or naked R+) should be used for comparison with the presented experimental findings.

Experimental IR spectra and properties of the carborocations

The CH3+ cation has an extremely high ability to bind to the bases. Even in the CH3{Fl11−} compound with the weakest basic ion {Fl11−}, the methyl group forms a highly polar covalent bond.33

The CH3+ cation is the most convenient object for evaluating the influence of the polarization effect on charge scattering over the methyl group in the absence of hyperconjugation.

Polarization is responsible for the transfer of some electron density from hydrogens to the central carbon. This effect leads to an increase of the CH stretch frequencies and strengthening of the force constants of CH bonds.33 Thus, the methyl group in the absence of hyperconjugation.

The IR spectrum of the ethyl carborane, C2H5[Cl11], revealed another extreme case:32 all C–H stretch frequencies are in the region 2933–3057 cm⁻¹ indicating covalent binding between C2H5 and {Cl11} moieties, which prevents the hyperconjugation effect. The frequencies of the CH2 group of C2H5{Cl11} (3057 and 2976 cm⁻¹) are slightly higher than those of the chloronium cation (C2H5)2Cl+ (3038 and 2974 cm⁻¹), pointing to the more polar C–Cl bond in the case of C2H5[Cl11].

The C2H5+ cation was obtained in the form of ionic salt C2H5+[Fl11−]. Its formation through an unstable salt of fluoronium cation, (CH3)3F+, is accompanied by the formation of i-Pr+.33 IR spectra showed the bands of both cations, whose intensities vary depending on the ratio of cations (Fig. 2a). Obtaining the difference between the spectra of the samples with a low and high portion of i-Pr+ (Fig. 2b, red and black)—up to full compensation of the absorption from i-C3H7+—allowed us to obtain a spectrum of the C2H5+ cation (Fig. 2b). Reverse subtraction of the spectra (‘‘black’’ minus ‘‘red’’) did not fully remove the spectrum of the

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**Fig. 2** IR spectra of (a) a mixture of C2H5+[Fl11−] and i-Pr+[Fl11−] salts,33 showing the transformation of C2H5+ into i-Pr+ (red-blue-black); (b) the C2H5+ cation spectrum obtained by subtracting the black spectrum (a) from the red spectrum (a) until full compensation of the band at 2831 cm⁻¹ of i-Pr+; (c) the i-C3H7+ spectrum isolated by reverse subtraction of the spectra: black (a) minus red (a). An uncompensated remnant from C2H5+ absorption is marked by an asterisk. The bands 3078 and 2960 cm⁻¹ belong to the methyl group of the unreacted CH3[Fl11] salt. The strong band, marked with **, belongs to the {Fl11−} counterion.
The patterns observed in the IR spectra of the carbocations

\[ \text{C}_2\text{H}_5^+ \text{ cation} \] but allowed us to see the main features of the \( \text{i-C}_3\text{H}_7^+ \) spectrum (Fig. 2c). The absorption contour of CH stretches affected by hyperconjugation is asymmetric for both cations and can be broken down into at least two components (Fig. 2b and c).

The IR spectrum of the \( \text{i-C}_3\text{H}_7^+ \{\text{F}_{11}^-\} \) salt obtained in reaction (1) differs from the spectrum shown in Fig. 2c. This means that two isomers of \( \text{i-C}_3\text{H}_7^+ \) can form. This issue will be discussed below.

We did not succeed in obtaining a high-quality spectrum of the \( \text{i-C}_3\text{H}_7^+ \{\text{Cl}_{11}^-\} \) salt according to eqn (3) because formation of this salt is accompanied by formation of the chloronium cation (\( \text{C}_3\text{H}_7^+\{\text{Cl}^-\} \)). Superimposition of the two spectra allowed us to determine only the maximum of the absorption from the C–H stretches of \( \text{i-C}_3\text{H}_7^+ \) disturbed by hyperconjugation (Fig. S8 in ESI†).

The \textit{cyclo}-\textit{pentyl} cation. A white powder of the \textit{cyclo}-\textit{C}_3\text{H}_7^+\{\text{F}_{11}^-\} salt obtained \textit{via} direct interaction of acid \( \text{H}\{\text{F}_{11}\} \) with \textit{cyclo}-pentane (eqn (2)) yielded a high-quality IR spectrum (Fig. 3). Nevertheless, the \textit{cyclo}-\text{C}_3\text{H}_7^+\{\text{Cl}_{11}^-\} salt did not form in a similar manner. It was obtained in the reaction of \( \text{H}\{\text{Cl}_{11}\} \) with \textit{cyclo}-pentane; this reaction was accompanied by formation of oligomeric carbocations, which are degradation products of the intermediately chloronium cations decomposing at room temperature. In Fig. 4, the IR bands from these byproducts are marked with asterisks. The important region of CH stretches of the \textit{cyclo}-\text{C}_3\text{H}_7^+ cation, which was disturbed by hyperconjugation, was not distorted by impurities, and separation of their bands into individual components became possible.

The patterns observed in the IR spectra of the carbocations

\( \text{i-Bu}^+ \) is the most actively studied carbocation. On the basis of experimental data from the gaseous and condensed phase experiments, two \( \text{CH}_3 \) groups of the \( \text{i-Bu}^+ \) cation were proven to be involved in hyperconjugation. All three CH bonds of each group donate \( \sigma \)-electrons to the 2p orbital of the sp\(^2\) C atom (Scheme 2) and their CH stretches appear in IR spectra as group vibrations, \( \nu_{\text{asCH}_3} \) and \( \nu_{\text{CH}_3} \), with significantly decreased frequencies (at 2867, 2822 and 2771 cm\(^{-1}\)) in the case of the salt with \( \{\text{Cl}_{11}^-\} \) counterion, Fig. 5a). The third CH group (marked as \( \text{CH}_3^\# \)) is predominantly polarized and shows three higher-frequency bands in the gas phase. This observation is supported by important experimental evidence: the stretch vibrations of \( \text{CH}_3 \) and \( \text{CH}_3^\# \) groups in \( \text{i-Bu}^+ \) show a good correlation (Table 2), which confirms their attribution to group vibrations and indicates that both types of \( \text{CH}_3 \) groups are isoelectronic.

| Group          | \( \nu_{\text{asCH}_3} \) (cm\(^{-1}\)) | \( \nu_{\text{CH}_3} \) (cm\(^{-1}\)) |
|----------------|---------------------------------|---------------------------------|
| \( \text{CH}_3^\# \) | 3038                            | 2965                            |
| \( \text{CH}_3 \)  | 2880                            | 2839                            |
| Ratio          | 1.055                           | 1.044                           |

In addition, the C–H stretch frequencies of \( \text{i-Bu}^+ \) involved in hyperconjugation very well correlate with those of the isoelectronic planar trimethyl boron (\( \text{CH}_3 \)\)\text{"B\(^7\)} (Table 3). This observation confirms that the types of local \( \text{CH}_3 \) normal vibrations for both compounds coincide, and the electron distributions in their methyl groups are identical.

Finally, a good correlation was also observed between the frequencies of the \( \text{CH}_3^\# \) group in \( \text{i-Bu}^+ \) and those of the strongly polarized methyl group in \( \text{CH}_3\{\text{F}_{11}\} \) (Table 4), confirming the above-mentioned conclusions.

In the condensed phases, \( \text{i-Bu}^+ \) forms noticeable H-bonds with the nearest surroundings favoring involvement of the \( \text{CH}_3^\# \) group in hyperconjugation, which is, however, weaker than that formed by its other two \( \text{CH}_3 \) groups. This phenomenon is accompanied by enhanced dynamic properties of the H atoms of \( \text{CH}_3^\# \), resulting in collapse of the three bands of \( \text{CH}_3^\# \) vibrations into one broad absorption (with an intensity of ca. 30% of that from all CH stretches) at a lower frequency (Fig. 5a).

The spectrum of i-Pr\(^+\) obtained in reaction (1) differs from that shown in Fig. 2b, but it is very similar to the spectrum of \( \text{i-Bu}^+ \) (Fig. 5). It shows a broad absorption pattern at 2922 cm\(^{-1}\)
with intensity \( \text{ca. 50\% of the total intensity of the CH stretch vibrations of i-Pr}^+ \). The three bands at a lower frequency belong to the second CH\(_3\) group involved in stronger hyperconjugation (the ratio of their intensity values may change, depending on the conditions of separation of the bands, but the number of bands is always three). Thus, the above-mentioned i-Pr\(^+\) isomer is an analog of \( \text{t-Bu}^+ \), with similar asymmetry, and will be designated as i-Pr\(_{\text{as}}^+\).

The spectrum of the second i-Pr\(^+\) isomer contains only two bands of CH\(_3\) groups involved in hyperconjugation (the third band was obviously not resolved) without the broad absorption (Fig. 2c). Thus, both CH\(_3\) groups equally participate in hyperconjugation. Hereinafter, we will refer to this symmetrical isomer as i-Pr\(_{\text{sym}}^+\).

The frequencies of hyperconjugated CH\(_3\) groups for both i-Pr\(^+\) isomers are close (Fig. 2c and 5b), which means that i-Pr\(_{\text{as}}^+\) and i-Pr\(_{\text{sym}}^+\) have roughly equal energy. Therefore, the efficiency of the positive charge redistribution over the CH\(_3\) and CH\(_3^*\) groups in carbocations is energetically equivalent.

A charged C\(_3\) core of the cyclo-C\(_5\)H\(_9^+\) cation is similar to that of i-Pr\(_{\text{sym}}^+\). Its IR spectrum does not contain the broad absorption pattern (Fig. 3), indicating that this cation is symmetric. CH stretches of the two equivalent CH\(_2^*\) groups involved in hyperconjugation (Scheme 5) result in two low-frequency bands at 2836 and 2765 cm\(^{-1}\). The remote CH\(_2\) groups yield the bands \( \nu_{\text{as}} \) at 2956 and \( \nu_{\text{s}} \) at 2904 cm\(^{-1}\). Moreover, the ratio of frequencies for these bands coincides (Table 5). This finding implies identical assignment of frequencies for CH\(_2^*\) and CH\(_2\) groups and their isoelectronic character, as established for two types of CH\(_3\) groups of t-Bu\(^+\) (Table 2). This result leads to a major conclusion: both CH bonds of CH\(_2^*\) groups equally donate \( \sigma \)-electrons to the 2p\(_z\) orbital of the sp\(^2\) C atom, in agreement with the case of t-Bu\(^+\).

The C\(_2\)H\(_5^+\) spectrum shows two bands from the CH\(_3\) group vibrations, which are similar to those observed in the i-Pr\(_{\text{sym}}^+\) spectrum (Fig. 2b and c). The broad absorption pattern, of course, is absent. This finding points to some generic relation between C\(_2\)H\(_5^+\) and i-Pr\(_{\text{sym}}^+\). The overall picture of the generic relations between the analyzed carbocations with hyperconjugative stabilization is shown in Fig. 6.

One can see that there are two kinds of carbocations: (i) carbocations with one type of hyperconjugated CH\(_3\)/CH\(_2\) groups

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**Table 3** Comparison of experimental CH stretches of t-Bu\(^+\) with those of isoelectronic (CH\(_3\))\(_3\)B\(^{27}\) (in cm\(^{-1}\))

| Group          | \( \nu_{\text{as}}\text{CH}_3 \) | \( \nu_{\text{s}}\text{CH}_3 \) |
|----------------|----------------------------------|----------------------------------|
| t-Bu\(^+\) gas | 2880                             | 2839                             |
| (CH\(_3\))\(_3\)B gas | 2900                             | 2875                             |
| Ratio          | 0.960                            | 0.954                            |

**Table 4** Comparison of experimental CH stretches of the polarized CH\(_3^*\) group of t-Bu\(^+\) with those of the CH\(_3\)(F\(_{11}\)) compound (in cm\(^{-1}\))

| Group          | \( \nu_{\text{as}}\text{CH}_3 \) | \( \nu_{\text{s}}\text{CH}_3 \) |
|----------------|----------------------------------|----------------------------------|
| t-Bu\(^+\) gas | 3038                             | 2965                             |
| CH\(_3\)(F\(_{11}\)) solid | 3098                             | 3086                             |
| Ratio          | 0.981                            | 0.961                            |

**Table 5** CH stretch frequencies (in cm\(^{-1}\)) of the cyclo-pentyl cation

| Group          | \( \nu_{\text{as}}\text{CH}_2 \) | \( \nu_{\text{s}}\text{CH}_2 \) |
|----------------|----------------------------------|----------------------------------|
| CH\(_3^*\)     | 2836                             | 2765                             |
| CH\(_3^0\)     | 2956                             | 2904                             |
| Ratio          | 0.959                            | 0.952                            |

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**Scheme 5** Schematic representation of the cyclo-pentyl cation.
(C₂H₅⁺, i-Pr⁺, and t-Bu⁺), which form a symmetrical C₃ charged core; (ii) carbocations with an asymmetrical C₃ or C₄ charged core formed by two types of CH₃ groups.

The frequencies of the CH₃/CH₂ groups mostly affected by hyperconjugation for all carbocations under study are summarized in Table 6. The decrease in the frequencies from {F₁₁} to {Cl₁₁} salts is due to the formation of H-bonds.¹⁷

All CH stretch vibrations of C₂H₅⁺, i-Pr⁺, cyclo-pentyl⁺, and t-Bu⁺ cations were observed in IR spectra with the exception of those from CH₂ and CH groups at the sp² C atom in C₂H₅⁺ and i-Pr⁺, respectively, which are weak and located in the frequency region of the intense C–H stretches from {F₁₁} or {Cl₁₁} anions.

Experimental data versus calculations. Experimental and calculated data showed that the impact of the environment on the nature of the R–{F₁₁} bond may be significant. The CH₃ group is linked covalently to {F₁₁}, and the calculated CH₃ frequencies (both for vacuum and for the condensed phase) are in good agreement with the empirical ones for solid CH₃–{F₁₁} (Table S3, ESIF). When R is C₂H₅ and larger, the ionicity of the C–F bond and the hyperconjugated effect in compounds R{F₁₁} gradually increase in the series R = C₂H₅, i-C₃H₇, cyclo-C₅H₉, and t-Bu. Nonetheless, the experiments showed that starting from R = C₂H₅ (and larger), the compounds are purely ionic (Table 7). In the case of the more basic {Cl₁₁} carborane, an abrupt switch from the covalent to ionic state takes place between C₂H₅{Cl₁₁} and i-C₃H₇{Cl₁₁}. For the more basic CHB₁₁Me₅Br₆⁻ the switch “covalent–ionic state” occurs between i-C₃H₇{Cl₁₁} and t-C₅H₉{Cl₁₁}, which form a symmetrical C₃ charged core; (ii) carbocations with an asymmetrical C₃ or C₄ charged core formed by two types of CH₃ groups.

| Cation             | Anion        | νCH₃/νCH₂     |
|--------------------|--------------|--------------|
| C₂H₅⁺              | {F₁₁}        | 2791         |
| i-Pr⁺              | {F₁₁}        | 2874         |
| t-Bu⁺              | {F₁₁}        | 2866         |
| Cyclo-pentyl⁺       | {Cl₁₁}       | 2830         |
| i-Pr⁺              | {Cl₁₁}       | 2780         |
| t-Bu⁺              | {Cl₁₁}       | 2791         |
| Cyclo-pentyl⁺       | {Cl₁₁}       | 2777         |

The most intense bands are boldfaced. * Not determined.

Table 7 The covalent and ionic R–X compounds (X = carborane) identified on the basis of the presence or absence of the strong hyperconjugation effect during R stabilization.

| Carborane, X | Covalent compounds, R–X | Ionic salts, R⁻X⁻ |
|--------------|--------------------------|------------------|
| {F₁₁}        | H₃C–X                    | R = C₂H₅ and larger |
| {Cl₁₁}       | H₃C–X, C₂H₅–X            | R = i-C₃H₇ and larger |
| CHB₁₁Me₅Br₆⁻ | H₃C–X, C₂H₅–X, i-C₃H₇–X | R = t-C₅H₉ and larger |

The most intense bands are boldfaced. * Not determined.
two for i-Pr⁺, and three for t-Bu⁺. The experiments imply that these numbers are 2(3), 3 and 3 respectively. (4) The calculated splitting of the bands is rather small (13–17 cm⁻¹) and cannot be detected in the condensed-phase IR spectra because the corresponding bands should be merged into one slightly broadened (degenerated) band. In contrast, experimental spectra show three common bands for CH₃ group vibrations separated by 96 cm⁻¹.

A comparison of the calculated frequencies for the cyclo-pentyl⁺ cation (C₂ symmetry) with the experimental spectrum of cyclo-C₅H₅⁺[F₁₁⁻] revealed (Fig. 3) that there is also a significant discrepancy between theory and experiment, as in the case of C₅H₅⁻ and i-Pr⁺ cations. From the experimental spectrum it follows that both CH bonds of the CH₃⁺ group of cyclo-pentyl⁺ are equally influenced by hyperconjugation, and CH₂⁺ and CH₃⁺ are isoelectronic and have the same type of normal vibrations. The same is true for t-Bu⁺ (and i-Pr⁺⁺⁺⁺): three C–H bonds of CH₃ are equally involved in hyperconjugation, and both CH₃ and CH₃⁺ groups are isoelectronic, with the same type of local group vibrations. Unfortunately, these results contradict computational data.

To try to reconcile the quantum-chemical calculations with the experiment, we performed PBE-D3 computations with periodic boundary conditions for the t-Bu⁺[Cl₁₁] crystal lattice previously determined by X-ray crystallography.¹⁷ No significant structural changes were found in the fully relaxed unit cell, as compared to the experiment. In contrast, the calculated vibrational frequencies of t-Bu⁺ in the crystal lattice were found to have the same features as those in gaseous t-Bu⁺ (Table S5 in ESI†), which again contradict the experimental findings. Similar results follow from the calculations when experimental atomic coordinates were used without relaxation (Table S5 in ESI†). Thus, the origin of inconsistencies in the mechanisms of carboxylation hyperconjugation stabilization that follow from calculations and experiments has yet to be established.

**Conclusions**

According to the experiment, two sets of carbocations exist: with a symmetric and an asymmetric charged core. Our DFT calculations predict no carbocations with an asymmetrical charged core and their results in general contradict the experimental data.

The standard theoretical representation of the mechanism of hyperconjugation predicts that σ-electron density is transferred to the empty 2p₂ orbital of the sp² C atom from one preferred CH⁺ bond of each CH₃ group. At the same time, the σ-electron density on the other CH⁺ and CH⁺ bonds slightly increases (Scheme 1). It looks like σ-electrons of the three C–H bonds of the CH₃ group do not merge into molecular orbitals with the generalized electrons. This phenomenon manifests itself in calculated IR spectra, including high-level CCSD(T) computations,¹⁸ as a strong reduction in the ν(CH⁺) frequency (much stronger than in the experiment) making it highly characteristic. Accordingly, vibrations of C–H' and C–H'' bonds also appear to be highly characteristic ones, which are not mixed with those of the CH⁺ bond. To the best of our knowledge, this case is unknown in the practice of vibrational spectroscopy.

From the experimental data it follows that donation of the σ-electrons from the CH⁺ bond to the empty 2p₂ orbital of the sp² C atom is accompanied by an equal withdrawal of the electron density from C–H' and C–H'' bonds. That is, the electrons are supplied from each CH bond of the CH₃ group, and the C–H⁺ bond does not act as the predominant donor. Thus, all three bonds of CH₃ groups are equivalent. As a result, the CH stretches manifest themselves as typical CH₃ group vibrations with a smaller red shift (~60–100 cm⁻¹) as compared with that predicted by calculations for CH⁺ stretches (100–200 cm⁻¹). The vibrations of the stronger polarized CH₃⁺ group also appear to be common CH₃ group vibrations with equivalent C–H bonds.

Because calculations revealed that the impact of hyperconjugation on the CH₃ group weakly depends on the dihedral θ angle (the CH₃ rotation around the C–C bond), the donation of the σ-electron density from CH₃ to the empty 2p₂ orbital of the sp² C atom may take place not only via the C–H⁺ bond, but also via CH' and CH'' bonds. This mechanism is indicated in Scheme 2 by a dashed arrow.

The aforementioned inconsistencies are valid for all quantum-chemical calculations of naked carbocations known to date. Furthermore, our DFT calculations for the t-Bu⁺[Cl₁₁] and R[Hal₁₁] molecular compounds in a DCE solution turned out to be comparable with those for naked carbocations, leading to the generally accepted mechanism of hyperconjugative stabilization rather than the mechanism deduced from our experiments.

We can hypothesize that fine electronic structure of carbocations that has not yet been taken into account may be responsible for the observed theory-versus-experiment discrepancies. It seems that potential energy surfaces of the carbocations under study are more complicated than expected and cannot be analyzed by the standard quantum-chemical methods such as conventional DFT. This is the subject of our ongoing research.

Undoubtedly, further computational studies in this field, possibly based on the more advanced methods, will result in convergence of the theory with experiment and will allow researchers to explain a number of recently detected features of carbocations, such as the energy equivalence of the CH₄ and CH₃⁺ groups in asymmetric carbocations; why increasing the number of methyl groups from two (i-Pr⁺) to three (t-Bu⁺) does not influence the frequencies of C–H stretches; and the abrupt change in the state of the CH₃⁺ group when t-Bu⁺ is transferred from gaseous to condensed phases.²⁸

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