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Thermodynamic Stabilities of Carbocations

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Dedicated to Professor Edward M. Arnett

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1 Introduction

Small ions such as methylium (CH_3^+), methanium (CH_5^+) and ethylium (C_2H_5^+)^{1,2} are long-time favorites of experimental chemical physicists and theoretical chemists. Some of their work is reflected in this chapter. Furthermore, these and/or other cognate species such as vinylum (C_2H_3^+) and cyclopropenylium ($c\text{-C}_3\text{H}_3^+$) ions have been either detected or postulated to be significant constituents of the interstellar space³ and the stratospheres of the outer planets and some of their satellites^{4,5} as a result of the ionization of hydrocarbons.⁶ Even larger species have recently been considered.⁷ So, a great deal of experimental and computational information on their

structure, molecular spectra and energetics is available and part of it is summarized here. On the other hand, many of these species are far too reactive to be experimentally observed in solution, let alone the solid state. At the other end of the “stability spectrum” we have species such as substituted triarylmethyl cation, cyclopropenyl cation and tropylium ions, which form authentic hydrocarbon salts. A series of these and other remarkable carbocations has recently been reviewed.⁸ The cyclopropenyl cation and tropylium ions are aromatic species with highly delocalized π -electron systems.⁹

A number of carbenium ions lies between these two extremes, including secondary and tertiary alkyl carbocations as well as protonated aromatic hydrocarbons, many of them identified in solution, and more recently, as relatively stable solid salts (some representative examples are examined here). The study of all these species has long been a very important part of physical organic chemistry. Their industrial importance has promoted a great deal of research, both experimental^{10–15} and theoretical.^{16–20}

This chapter essentially addresses the following topics:

- (1) The quantification of the concept of “stability”. More precisely, thermodynamic criteria are applied in order to rank carbenium ions on the basis of their intrinsic stabilities, that is, stabilities in the absence of solvent. Both experimental and computational data are used.
- (2) The relationship between the intrinsic thermodynamic stability of these species and their reactivity in solution, from both the thermodynamic and the kinetic points of view.
- (3) Relevant structural features of these species, as revealed by experimental or computational methods data, are reviewed. Furthermore, quantum mechanical calculations at the highest possible levels (within our computational capabilities) were performed on most of these species. The scope of this chapter is limited to a relatively small number of ions that illustrate some representative examples of structural effects.

2 Quantitative thermodynamic criteria of stability in the gas phase

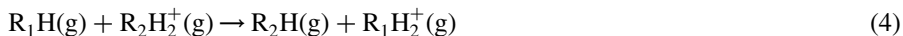
DEFINITIONS AND EXPERIMENTAL TECHNIQUES

We are concerned here with the thermodynamic stability of carbocations. For the sake of generality, we formally consider that they derive from a neutral molecule $R-H$, which can either lose a hydride or be protonated in the gas phase, reactions (1) and (2):



A quantitative ranking of stabilities for any two of these species (e.g., R_1^+ and R_2^+) can be defined through the thermodynamic state functions for the hydride- or proton-

exchange processes (3a) and (4):^{21,22}



The standard enthalpies and Gibbs energy changes for these reactions at some temperature T , respectively, $\Delta_r H^\circ_T$ and $\Delta_r G^\circ_T$, involve the corresponding standard magnitudes for the various reactants and products.

For example, the standard enthalpy change for reaction (3a) at 298.15 K is given by equation (3b):

$$\begin{aligned} \Delta_r H^\circ(3\text{a}) = & \Delta_f H^\circ_{\text{m}}[\text{R}_2\text{H}(\text{g})] + \Delta_f H^\circ_{\text{m}}[\text{R}_1^+(\text{g})] - \Delta_f H^\circ_{\text{m}}[\text{R}_1\text{H}(\text{g})] \\ & - \Delta_f H^\circ_{\text{m}}[\text{R}_2^+(\text{g})] \end{aligned} \quad (3\text{b})$$

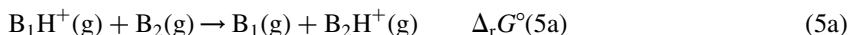
wherein the various $\Delta_f H^\circ_{\text{m}}$ terms are the standard enthalpies of formation of the various species involved in the reaction.

Experimental values of the standard enthalpies of formation of the neutral species, generally obtained by thermochemical or kinetic techniques,^{23–25} are frequently available and there are some excellent critical compilations of these data^{26–31} that can be eventually estimated empirically^{32–35} or computationally (see later).

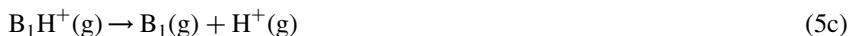
Several methods exist that allow the determination of the standard enthalpies of formation of the ionic species. The reader is referred to two recent rigorous and detailed chapters by Lias and Bartmess³⁶ and Ervin.³⁷ The vast majority of the experimental data reported here are obtained by means of Fourier transform ion cyclotron resonance spectroscopy (FT ICR), high-pressure mass spectrometry (HPMS), selected ion flow tube (SIFT), and pulsed-field ionization (PFI) techniques, particularly pulsed-field ionization photoelectron photoion coincidence (PFI-PEPICO). All these experimental techniques have been examined quite recently, respectively, by Marshall,³⁸ Kebarle,³⁹ Böhme,⁴⁰ Ng⁴¹ and Baer.⁴² These chapters appear in a single (remarkable) issue of the *International Journal of Mass Spectrometry*. An excellent independent discussion of the thermochemical data of ions, with a careful survey of these and other experimental methods, is given in Ref. 37.

From these techniques the following raw experimental data are obtained:

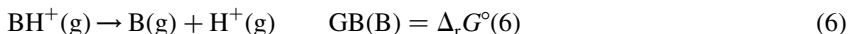
- (1) FT ICR, HPMS and SIFT yield the standard Gibbs energy change, $\Delta_r G^\circ(5\text{a})$ for reaction (5a), the proton exchange between two bases, B_1 and B_2 ,



$\Delta_r G^\circ(5\text{a})$ is given by the difference between $\Delta_r G^\circ(5\text{b})$ and $\Delta_r G^\circ(5\text{c})$ pertaining, respectively, to reactions (5b) and (5c):



The standard Gibbs energy change for reaction (6) is known as the gas-phase basicity of base B, GB(B):



From this it follows that the unknown GB of a base, say B₁, can be obtained from the experimental values of $\Delta_r G^\circ(5a)$ and GB(B₂), B₂ being an appropriate reference base.^{43,44}

- (2) SIFT and HPMS experiments performed at different temperatures provide the standard enthalpy change for reaction (5a), $\Delta_r H^\circ(5a)$. As before, combination of this datum with $\Delta_r H^\circ(5b)$ leads to $\Delta_r H^\circ(5c)$, also known as the proton affinity of B₁, PA(B₁).^{43,44}
- (3) Ionization techniques are extremely important sources of thermochemical data for ions. Excellent chapters are given in Refs. 37, 41 and 42.

Here, we simply consider that they yield (*inter alia*) the adiabatic ionization energies (IE) and appearance energies (AE) defined as the standard energy changes at 0 K for reactions (7) and (8) (assuming for the latter that there is no potential barrier in the reaction coordinate and little or no kinetic shift):



Extracting $\Delta_f H^\circ_m(\text{R}^+)$ or $\Delta_f H^\circ_m(\text{A}^+)$ at finite temperatures from IE or AE, respectively, requires the corresponding $\Delta_f H^\circ_m$ values for the appropriate neutral species as well as their corresponding integrated heat capacities. The latter can be obtained from compilations (see above) or else computed by quantum chemical methods. Several conventions, clearly presented and compared in Refs. 36 and 37, exist for the determination of $\Delta_f H^\circ_m(\text{e}^-)$. Here, we follow the so-called “ion convention” because it is used in a number of important sources of thermochemical data for ions. In this convention, the enthalpy of formation of the electron is defined as equal to its integrated heat capacity at all temperatures. Note that as indicated by Bartmess,^{45,46} the most rigorous approach is to treat the electron as a fermion and to apply Fermi–Dirac statistics to compute its integrated heat capacity and entropy. We suggest that institutions such as IUPAC ought to officially recommend this treatment.

Directly determined experimental standard entropies for carbenium ions in the gas phase, S°_m , are seldom available. Those we present here are derived generally from the combination of experimental gas phase $\Delta_r G^\circ_m$ and $\Delta_r H^\circ_m$ values. We also report the data obtained by quantum mechanical methods. A careful discussion of these data is given in Ref. 47. When needed, S°_m values for neutral species were taken from compilations^{29,30,48} or computed.

THE SPECIFIC CASE OF CARBOCATIONS

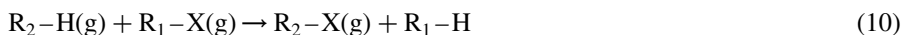
Hydride, halide and proton exchanges

The quantitative ranking of stabilities can sometimes be obtained directly by HPMS or FT ICR. In both these cases the main condition is the absence of isomerization or other extraneous processes.

Carbocations can exchange hydride, as in reaction (3a),⁴⁹ or halide anions (mostly chlorides and bromides),⁵⁰ as in reaction (9):

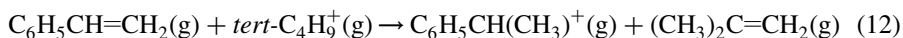
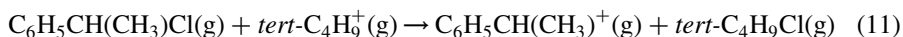


As we show below, exchanges of other species can be studied, at least formally. In all cases, the rankings defined through equations (3a) and (9) are linked through equation (10):



This is an isodesmic process involving the neutral species only. In principle, $\Delta_f G^\circ(10)$ and $\Delta_f H^\circ(10)$ can be obtained experimentally. Otherwise, this “leaving group correction” can be obtained by quantum chemical calculations. Here, we use both methods.

Equilibrium proton exchange between ethylenic compounds is ideally suited whenever isomerization and/or other processes cannot compete with proton exchange. If contributions from the neutral species are very small, rankings obtained by this method and by chloride exchange are essentially identical. For example, the standard Gibbs energy changes for reactions (11) and (12) are, respectively,⁵¹ -7.7 and -7.5 kcal mol⁻¹:



Other important examples are also known.⁵²

The dissociative proton attachment method

The construction of a quantitative scale of carbocation stabilities based on hydride or halide exchanges would require the systematic overlapping equilibration⁴⁴ of a large number of species (as in reactions (11) and (12)). This was the time-honored procedure for the construction of the gas-phase proton basicity scale.⁴³ In the present case, this is difficult to achieve because of the widely different stabilities involved and because of the possibility of rearrangement of the ions.

It has long been known that in the gas phase, R-X compounds (X = OH, halogen, SH, etc.) can react with protonated bases, BH⁺, to undergo a “dissociative proton

attachment process" (DPA), as shown in reaction (13):



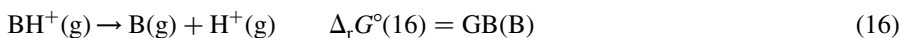
Lias and Ausloos⁵³ have summarized earlier literature on these processes.

We have recently shown that by varying the strength of the bases (B), it is possible to determine the onset for reaction (13) fairly accurately.⁵⁴ This is conveniently done by means of FT ICR. Full experimental details are given in Refs. 54 and 55. Briefly stated, $\text{BH}^+(\text{g})$ is formed by chemical ionization following the electron ionization of a mixture of $\text{B}(\text{g})$ and $\text{R}-\text{X}(\text{g})$ (in general, fragment ions from B and/or $\text{R}-\text{X}$ act as proton sources) and then isolated by ion ejection techniques and allowed to react. The formation/absence of $\text{R}^+(\text{g})$ is monitored for periods ranging from 1 to (sometimes) 60 s.

The dissociative proton transfer from $\text{BH}^+(\text{g})$ to $\text{R}-\text{X}$ under a pressure P , reaction (13), will take place spontaneously (assuming a negligible dissociation barrier) when $\Delta_r G^P(13) < 0$. It can be easily shown that $\Delta_r G^P(13)$ is given by equation (14):

$$\Delta_r G^P(13) = \Delta_r G^P(15) + \Delta_r G^P(16) \quad (14)$$

wherein $\Delta_r G^P(15)$ and $\Delta_r G^P(16)$ pertain, respectively, to reactions (15) and (16):



The experimentally determined onset for reaction (13) satisfies the condition $\Delta_r G^P(13) \approx 0$. It then follows that $\Delta_r G^P(15) \approx -\Delta_r G^P(16)$.

Let R_1-X and R_2-X , respectively, stand for two halides (or alcohols or other derivatives) and B_1 and B_2 two reference bases defining their respective DPA onsets. The position of equilibrium (17) as determined by $\Delta_r G^\circ(17)$ is a quantitative measure of the relative stabilities of $\text{R}_1^+(\text{g})$ and $\text{R}_2^+(\text{g})$:



It can be readily shown that $\Delta_r G^\circ(17) = \Delta_r G^P(17)$. Then, and from the discussion given above, equation (18) follows:

$$\Delta_r G^\circ(17) \approx \text{GB}(\text{B}_2) - \text{GB}(\text{B}_1) \quad (18)$$

This expression reduces the determination of the relative stabilities of $\text{R}_1^+(\text{g})$ and $\text{R}_2^+(\text{g})$ through the formal exchange of the halide, hydroxide or other anions, reaction (17), to the actual determination of the DPA onsets for the corresponding neutral precursors, reaction (13).

These are bracketing experiments and their precision (estimated at *ca.* 2 kcal mol⁻¹) is lower than that achieved under "true" equilibrium conditions. They have, however, the following advantages: (1) ions are formed under extremely mild conditions (see later); (2) the acidity of the protonating species $\text{BH}^+(\text{g})$ can be varied within very wide limits by an appropriate choice of $\text{B}(\text{g})$; (3) gas-phase basicities are available for hundreds of compounds.

Over the last several years, the DPA method has been applied to a number of systems. The following illustrates its scope and the reliability of the data derived therefrom.

- (1) We have applied DPA to *tert*-butyl and *sec*-butyl chlorides.^{55,56} As discussed in other sections, the difference in stabilities we obtained was in excellent agreement with that provided by other methods. The most important point, however, is that the DPA onset for *sec*-BuCl could be clearly determined, in spite of the fact that *sec*-Bu⁺ readily rearranges to *tert*-Bu⁺. This is explained by the fact that the DPA are *entropy-driven, endoergic reactions*. This makes DPA extremely valuable for the study of relatively unstable species.^{55,57,58} Examples of such processes are known.^{59–61} They are currently under study in our laboratories.
- (2) We have applied DPA to a set of halomethanes.⁶² A value of $201.9 \pm 2.0 \text{ kcal mol}^{-1}$ for $\Delta_f H_m^\circ(\text{CCl}_3^+)$ was obtained from that study.^{63,64} From the most recent $\Delta_f H_m^\circ$ and adiabatic ionization energy for the trichloromethyl radical, respectively, $17.0 \pm 0.6 \text{ kcal mol}^{-1}$ ¹⁶⁵ and $8.06 \pm 0.02 \text{ eV}$,⁶⁶ one gets $\Delta_f H_m^\circ(\text{CCl}_3^+) = 202.7 \pm 0.8 \text{ kcal mol}^{-1}$. Using instead the computed ionization energy (CEPA-1 level with triple- ζ equivalent basis set) of 7.990 eV ,⁶⁷ $\Delta_f H_m^\circ(\text{CCl}_3^+)$ becomes $201.0 \pm 2.0 \text{ kcal mol}^{-1}$. Other examples exist showing that the accuracy of the thermodynamic data obtained by DPA is sufficient for the purposes of this study.
- (3) Consider reaction (17). For DPA results to be acceptable, one has to ensure that rankings of carbocation stabilities obtained by using different precursor species (i.e., different X) are self-consistent. For example, let us suppose we compare the stabilities of $\text{R}_1^+(\text{g})$ and $\text{R}_2^+(\text{g})$ through DPA studies of the respective chlorides and alcohols ($\text{X} = \text{Cl}$ and $\text{X} = \text{OH}$). The corresponding experimental $\Delta_r G^\circ(17)$ values are noted, $\Delta_r G^\circ(17, \text{X} = \text{Cl})$ and $\Delta_r G^\circ(17, \text{X} = \text{OH})$. They must satisfy equation (19):

$$\Delta_r G^\circ(17, \text{X} = \text{OH}) = \Delta_r G^\circ(17, \text{X} = \text{Cl}) + \Delta_r G^\circ(20) \quad (19)$$

wherein $\Delta_r G^\circ(20)$ pertains to reaction (20), an isodesmic process involving the neutral precursors and having the meaning of a leaving group correction:



We have recently reported results of a systematic DPA study of bridgehead carbocations using as precursors alcohols, chlorides and bromides.⁵⁸ Figure 1 is a plot of $\Delta_r G^\circ(17, \text{X} = \text{Br}, \text{calc. Cl})$, i.e., values of $\Delta_r G^\circ(17, \text{X} = \text{Br})$ obtained from experimental $\Delta_r G^\circ(17, \text{X} = \text{Cl})$ and corrected as indicated above, versus the experimental $\Delta_r G^\circ(17, \text{X} = \text{Br})$ and $\Delta_r G^\circ(17, \text{X} = \text{Br}, \text{calc. OH})$. It shows that the self-consistency is excellent.

The same was found to hold with a series of tertiary alkyl cations obtained from their chlorides and alcohols.⁶⁸

- (4) Reaction (3a) is one of the key reference processes used here. $\Delta_r G^\circ(3a)$ can also be obtained computationally. In keeping with previous studies, $\Delta_r G^\circ(3a)$ is

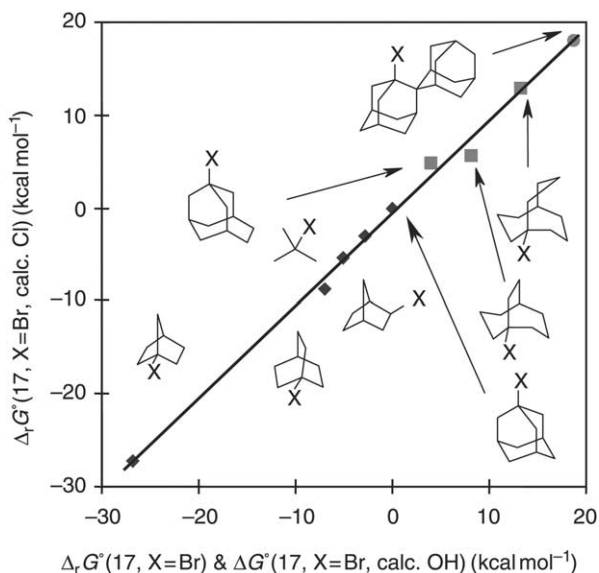


Fig. 1 Self-consistency of DPA results. Correction of leaving group effects.

referred to 1-adamantyl cation (R_2^+). A most stringent test of the self-consistency of the DPA method is the comparison of the $\Delta_r G^\circ(3a)$ values derived from experiment (upon the appropriate leaving group correction) with those obtained by purely computational methods (ranging from MP2(full)/6-31G(d) to G2(MP2) levels). [Figure 2](#) is an example of the quality of the agreement.

3 Theoretical calculations

Enthalpies and Gibbs free energies for the experimental processes of the systems involved were evaluated using high-level *ab initio* calculations. The results reported herein are based on G2⁶⁹ calculations for the smallest systems (up to five heavy atoms) and G2(MP2)⁷⁰ for the intermediate ones (between six and eight heavy atoms). Larger systems were optimized at the MP2(full)/6-31G(d) level. Thermodynamic corrections were generally calculated at the RHF/6-31G(d) level, with the scaling used in the G-n family of calculations. Thus, the results obtained for all the molecules can be compared at the same level, if necessary, since the calculations at the lowest levels are embedded in the G2 and G2(MP2) methodologies. In the same way, calculations at lower levels can be upgraded easily when the necessary computational resources become available.

The G2 and G2(MP2) computational methods used here provide molecular energies with deviations from the experimental data similar, in many cases, to the

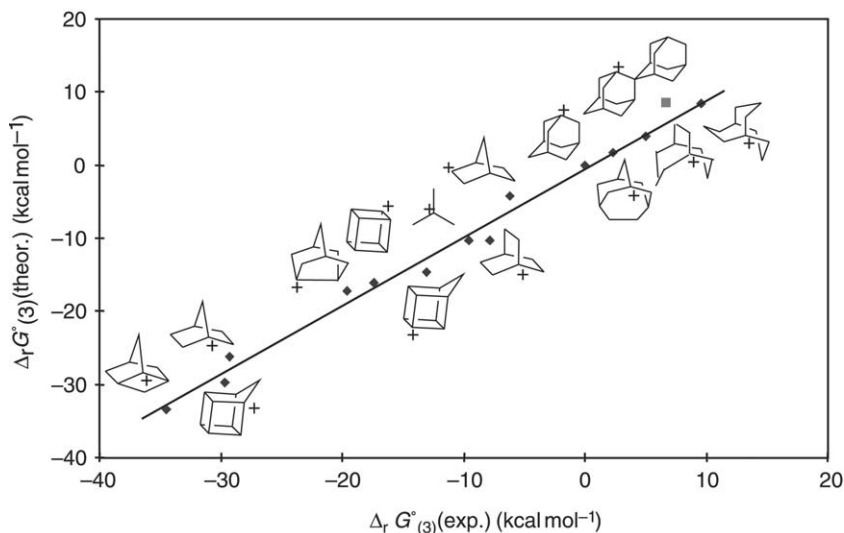


Fig. 2 Computed Gibbs energy changes for reaction (3a) versus DPA-based results.

accuracy of the latter. The reported average deviations are 1.21 and 1.52 kcal mol⁻¹ for the G2 and G2(MP2) calculations, respectively.^{69,70}

4 Uncertainties

From the inspection of reactions (3a), (4), (7) and (8), it follows immediately that the uncertainties on the standard enthalpies of formation of gaseous ions are determined by those affecting the thermochemical data for the relevant neutral species (molecules or free radicals) and the specific method used for ion generation. The uncertainty assigned to the standard enthalpy of formation of a gaseous ion is the root-sum-of-squares combination of the individual uncertainties of the various contributions.⁴³

Perusal of the data presented in the following sections would show that extremely accurate (better than 0.01 kcal mol⁻¹) ionization energies can be obtained with state-of-the-art optical spectroscopy and photoionization and electron ionization techniques.

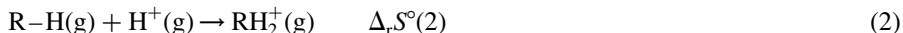
The uncertainties affecting experimental *differences* in GB values as determined by equilibrium methods are frequently in the range 0.1–0.3 kcal mol⁻¹. Individual differences in PA values obtained by van't Hoff plots of equilibrium constants for processes such as proton or halide exchange reactions are accurate to within a 1–2 kcal mol⁻¹ range as indicated by Kebarle and co-workers.⁷¹ The usual multiple-overlap technique likely halves these uncertainties in the case of data originating in the same laboratory. As indicated in the discussion of reactions (5a) and (6),

“absolute” GB and PA values must be anchored to some specific reference values. Overall, and unless warranted by other evidence, we take the accuracy of “absolute” GB and PA values as *ca.* 2 kcal mol⁻¹.⁴³ In many cases this is practically the main contributor to the uncertainty on $\Delta_f H_m^\circ$ values for ions. Note, however, that in some cases this is perhaps too conservative an estimate, in view of the excellent level of agreement that often exists between independent $\Delta_f H_m^\circ$ values obtained from ionization and equilibrium techniques.

DPA onsets are estimated to be known within 2 kcal mol⁻¹. These values must also be anchored to some reference. This leads to an estimated uncertainty of *ca.* 2.8 kcal mol⁻¹ on the formal $\Delta_f G_m^\circ(17)$ values. Furthermore, in order to extract $\Delta_f H_m^\circ$ values for ions, leaving group and entropy corrections are needed. With few exceptions, and because of the scarcity of experimental data, these corrections are determined computationally by means of isodesmic reactions.^{57,58,68} We estimate that the leaving group correction introduces an extra 1 kcal mol⁻¹ uncertainty. Unless otherwise stated, we anchor DPA onsets obtained from chlorides and alcohols to the onsets for the corresponding 1-adamantyl derivatives. We have recently introduced the DPA of methyl ethers as an appropriate tool for the study of very stable species (see later); their corresponding onsets are anchored to that for the methyl ether of tricyclopropyl carbinol.

Uncertainties on the experimental standard enthalpies of formation of neutral species vary widely. For most hydrocarbons and radicals they are in the 0.1–1.0 and 0.5–2.0 kcal mol⁻¹ ranges, respectively.

Very few standard entropies for ions relevant to this study are available that derive from purely experimental data. These data can be obtained, at least formally, from the combination of PA and GB values for processes such as reaction (2):



The accuracy of $\Delta_r S^\circ(2)$ is estimated at 1–2.5 cal mol⁻¹ K⁻¹. $S^\circ[\text{RH}_2^+(\text{g})]$ is even less accurate, because of the contribution from the uncertainty on $S^\circ[\text{RH(g)}]$.

A recent study⁴⁷ indicates that quantum mechanical calculations of moderate to high level are able to provide values of $\Delta_r S^\circ(2)$ accurate to within 0.3–0.6 cal mol⁻¹ K⁻¹. As regards the standard entropies for individual ions, we estimate that the accuracy of the scaled HF/6-31G(d) values used in the G-n family calculations^{69,70} (see above) is about 2 cal mol⁻¹ K⁻¹, based on the differences between values computed at this level and experimental or high-level computational data.

The accuracy of the data we present is not homogeneous and it is rather low in some cases, largely because of the unavailability of thermodynamic state functions for neutral species. Obviously, the spirit of this work is quite different from that of the excellent databases from NIST. Thus, while we have striven to provide the “best” possible thermodynamic values, we have also considered that even a “low-resolution” study of the relationships between structure, intrinsic (gas phase) stability and solution reactivity of carbocations is bound to provide useful results.

5 Thermodynamics and structure of selected species

CARBOCATIONS C1–C4

Methylum ion (CH_3^+) (**1**)

Spectroscopic studies in the gas phase^{72–76} and very high level *ab initio* calculations⁷⁷ indicate that this species is an oblate symmetric top belonging to the D_{3h} molecular point group (Fig. 3). The experimentally estimated C–H distance is 1.087 Å, the computed value (1.089 Å) being in excellent agreement.

The standard enthalpy of formation given in Table 1 is based on the experimental value of the adiabatic ionization potential of the methyl radical⁷⁸ and has been adjusted⁷⁹ to a series of fundamental enthalpies of formation. Very recently,⁸⁰ the onset of the formation of CH_3^+ from methane was determined quite accurately by means of the PFI-PEPICO technique. This datum, combined with other experimental results, yields the accurate 0 K dissociation energies (D_0) for CH_4 and CH_4^+ , $D_0(\text{H}-\text{CH}_3) = 103.479 \pm 0.023$ and $D_0(\text{H}-\text{CH}_3^+) = 39.321 \pm 0.092$ kcal mol⁻¹.

Methanium ion (CH_5^+) (**2**)

Reliable experimental values for $\text{PA}(\text{CH}_4)$ and $\text{GB}(\text{CH}_4)$ are available, particularly from HPMS and flowing afterglow studies.^{81,82} When combined with the (rather accurate) data for the neutral species, they provide the thermodynamic data given in Table 1. The results of G2 *ab initio* calculations (Ref. 83 and this study) are also reported.

Within the Born–Oppenheimer approximation, computational studies at extremely high levels^{84,85} show that the global minimum, **2a**(C_s), has a C_s symmetry and that it can be viewed as an H_2 molecule tightly bound to a methyl cation (three-center two-electron bonds). Two other structures, **2b**(C_s) and **2c**(C_v), respectively, of symmetries C_s and C_{2v} , are transition states. **2b**(C_s) involves the rotation of the H_2 moiety and allows the exchange of the two hydrogen atoms.

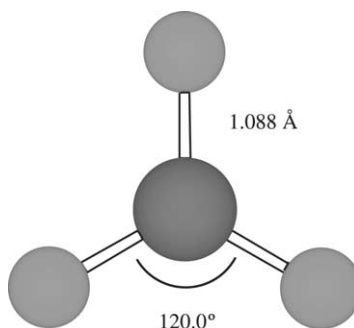


Fig. 3 Structure of methylum ion, **1**, optimized at the MP2(full)/6-31G(d) level.

Table 1 Thermodynamic data for selected carbocations, C1–C4

Cations	$\Delta_f H_m^\circ(\text{g})^a$	$S_m^\circ(\text{g})^b$
Methylum, CH_3^+ (1)	261.83 ± 0.06^c	44.59 ± 0.06^d
Methanium, CH_5^+ (2)	218.0 ± 2.0^e 220.3 ± 2.0^g	54.2 ± 1.2^f 53.8 ± 2.0^h
Ethylum, C_2H_5^+ (3)	215.6 ± 2.0^i 215.17 ± 0.50^k 215.25 ± 0.50^m 215.2 ± 2.0^n	55.2 ± 2.0^j 55.3 ± 2.0^l
Propan-2-ylum, <i>iso</i> - C_3H_7^+ (4)	193.04 ± 0.36^o 192.2 ± 2.0^q 192.7 ± 2.0^s 194.4 ± 2.0^t	68.0 ± 2.0^p 66.23 ± 0.24^r
Butan-2-ylum (<i>sec</i> -butyl), <i>sec</i> - C_4H_9^+ (5)	184.5 ± 1.3^u 182.4 ± 2.0^w 183.0 ± 2.0^y 183.4 ± 2.0^z	69.8 ± 2.0^v 71.2 ± 2.0^x
2-Methylpropan-2-ylum (<i>tert</i> -butyl), <i>tert</i> - C_4H_9^+ (6)	169.9 ± 0.9^{aa} 170.03 ± 0.26^{ac} 169.7 ± 0.6^{ae} 169.2 ± 1.7^{af}	73.4 ± 2.0^{ab} 74.04 ± 0.26^{ad}

^aIn kcal mol⁻¹.^bIn cal mol⁻¹ K⁻¹.^c $\Delta_f H_m^\circ(\text{g})$ from Ref. 79, based on the experimentally resolved threshold PE spectrum of CH_3 (Ref. 78) and vibrational data summarized in Chase, M. W., Jr. NIST-JANAF Thermochemical Tables, 4th edn (1998). J. Phys. Chem. Ref. Data, Monograph No. 9. The very high level calculation of the ionization energy of CH_3 (Ref. 77) agrees with experiment within 0.02 kcal mol⁻¹.^dObtained in this work using the smoothed experimental vibrational frequencies and C–H bond length given in Ref. 77.^eFrom the averaged experimental PA(CH_4) taken from Ref. 43 and $\Delta_f H_m^\circ(\text{CH}_4) = -17.80 \pm 0.10$ kcal mol⁻¹.²⁶^fFrom the experimental $S_m^\circ(\text{g})$ value for CH_4 , 45.09 ± 0.10 cal mol⁻¹ K⁻¹ (Ref. 26) and the recommended experimental values⁴³ for PA and GB(CH_4). Uncertainties are estimated from the differences between the experimental values determined.⁸¹^gFrom $\Delta_f H_m^\circ(\text{CH}_4)$ and the computed (G2) PA(CH_4), 127.6 kcal mol⁻¹ (this work).^hScaled, symmetry-corrected value from this work [HF/6-31G(d)].ⁱFrom the experimental PA(C_2H_4) = 162.6 kcal mol⁻¹ (Ref. 81) and $\Delta_f H_m^\circ(\text{C}_2\text{H}_4) = 12.54 \pm 0.25$ kcal mol⁻¹.²⁶^jFrom the experimental GB(C_2H_4) and PA(C_2H_4) from Refs. 43 and 81.^kFrom the adiabatic ionization potential of ethyl radical, 8.117 ± 0.008 eV determined by photoionization mass spectrometry⁹⁵ and $\Delta_f H_m^\circ(\text{C}_2\text{H}_5) = 28.35 \pm 0.41$ kcal mol⁻¹ from Ref. 96. Thermal corrections as in Ref. 95.^lFrom the *ab initio* scheme by Radom and co-workers.⁴⁷^mFrom PFI-PE spectroscopy and ion coincidence detection using multi-bunch synchrotron radiation.⁹⁷ⁿFrom the experimental $\Delta_f H_m^\circ(\text{C}_2\text{H}_4)$ and PA(C_2H_4) = 162.98 kcal mol⁻¹ computed at the G2 level.⁴⁷^oPFI-PEPICO TOF experiments and experimental $\Delta_f H_m^\circ(\text{g})$ for the various precursor species.¹⁰²^pFrom the experimental S_m° , (Ref. 26) PA and GB for C_3H_6 .

^gFrom the experimental PA of propene ($178.4 \text{ kcal mol}^{-1}$)⁸¹ and its $\Delta_f H_m^\circ(\text{g})$ value, $4.879 \text{ kcal mol}^{-1}$.²⁶

^h*Ab initio* computed value, from Ref. 47.

ⁱFrom the experimental $\Delta_f H_m^\circ(\text{g})$ of C_3H_6 and its G2-computed PA.^{47,83}

^jComputed (CBSQ, atomization).⁹⁹

^kFrom $\Delta_f H_m^\circ(\text{tert-C}_4\text{H}_9^+) = 169.9 \pm 0.9 \text{ kcal mol}^{-1}$ (see later) and the experimental enthalpy of isomerization $\text{sec-C}_4\text{H}_9^+ \rightarrow \text{tert-C}_4\text{H}_9^+$, $-14.55 \pm 0.50 \text{ kcal mol}^{-1}$.^{108,109} This value pertains to the formation of an equilibrating mixture of isomers **I** and **II** in solution.

^lScaled, symmetry-corrected value for structure **I**, computed at the MP2(full)/6-31G(d) level (this work).

^mFrom the experimental $\Delta_f H_m^\circ$ (Ref. 26) and $S_m^\circ(E\text{-C}_4\text{H}_8)$ ²⁹ and $\text{GB}(E\text{-C}_4\text{H}_8) = -172.5 \pm 1.1 \text{ kcal mol}^{-1}$ (Ref. 107) corrected with the computed S_m° values for structures **I** and **II**. This value pertains to the formation of an equilibrating mixture of isomers **I** and **II** in the gas phase.

ⁿScaled value for structure **II**, computed at the MP2(full)/6-31G(d) level (this work).

^oFrom the experimental $\Delta_f H_m^\circ(E\text{-C}_4\text{H}_8) = -2.58 \text{ kcal mol}^{-1}$ (Ref. 26) and the G2-computed $\text{PA}(E\text{-C}_4\text{H}_8)$ to yield structure **I** (this work).

^pFrom the experimental $\Delta_f H_m^\circ(E\text{-C}_4\text{H}_8)$ and the G2-computed $\text{PA}(E\text{-C}_4\text{H}_8)$ to yield structure **II** (this work).

^{aa}From PEPICO studies.¹¹³

^{ab}From the experimental $\text{GB}(\text{iso-C}_4\text{H}_8) = 185.4 \text{ kcal mol}^{-1}$ (Ref. 115) and $\text{PA}(\text{iso-C}_4\text{H}_8)$.⁸¹

^{ac}From photoionization mass spectrometry.¹¹⁴

^{ad}Computed value.⁴⁷

^{ae}From $\Delta_f H_m^\circ(\text{iso-C}_4\text{H}_8) = -4.29 \pm 0.26 \text{ kcal mol}^{-1}$, (Ref. 26) and $\text{PA}(\text{iso-C}_4\text{H}_8) = 191.7 \pm 0.5 \text{ kcal mol}^{-1}$.⁸¹

^{af}From the experimental $\Delta_f H_m^\circ$ and S_m° for $\text{iso-C}_4\text{H}_8$, from Ref. 26 and the calculated (G2) values for the PA and GB of $\text{iso-C}_4\text{H}_8$, respectively, 192.2 and $185.6 \text{ kcal mol}^{-1}$.^{47,83}

2c(C_v) allows the exchange between these hydrogens and those of the methyl tripod (Fig. 4).

These calculations also show that, in terms of electronic energies, structures **2b**(C_s) and **2c**(C_v) are some 0.1 and $0.8 \text{ kcal mol}^{-1}$ above structure **2a**(C_s). Inclusion of the vibrational contributions makes the barrier heights vanishingly small and raises some intriguing questions. In any case, these results suggest an extremely floppy structure and the possibility of easy scrambling of the hydrogen atoms.

Recently,^{86,87} CH_5^+ has been the subject of *ab initio* integral path calculations, which include nuclear quantum effects such as zero-point motion and tunneling in full dimensionality and go beyond the harmonic approximation. These studies confirm the above results, in that while protons undergo large-amplitude pseudorotational motion and become scrambled and statistically equivalent, this motion is concerted and the situations in which the vibrating nuclear skeleton having an H_2 moiety attached to a CH_3 tripod are the most important contributors to the overall appearance of the cation.

At this point, however, the situation is far from being entirely clear, because of the following facts:

- (1) The experimental (gas phase) IR spectrum of the C–H stretching region of CH_5^+ has been obtained.⁸⁸ It portrays some 900 lines and has not yet been interpreted.
- (2) Mass spectrometric studies⁸⁹ seem to indicate that, in the absence of intermolecular collisions, CH_4D^+ and CD_4H^+ do not show any rearrangement.

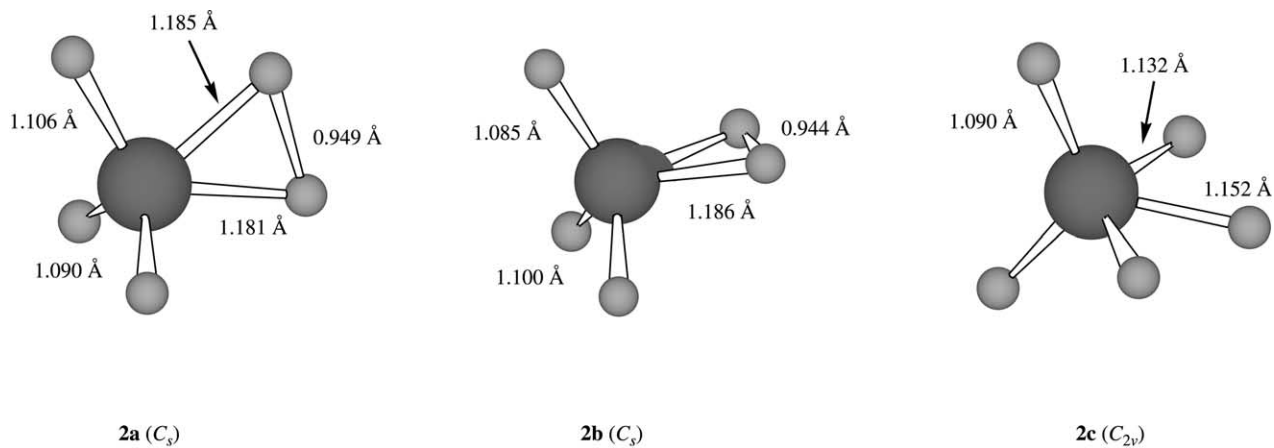


Fig. 4 Possible structures (Born–Oppenheimer approximation), for methanium ion, **2**, optimized at the MP2(full)/6-31G(d) level. **2a** is the absolute minimum; **2b** and **2c** are transition states.

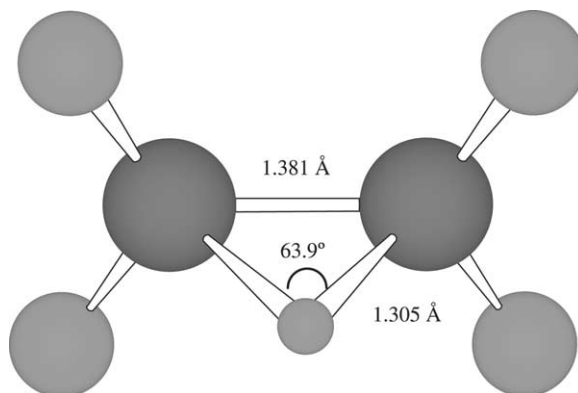


Fig. 5 Structure of ethylium ion, **3**, optimized at the MP2(full)/6-31G(d) level.

This situation has prompted a lively debate⁹⁰ but still remains a “tough test for experiment and theory”.⁹¹

*Ethylum ion, ethyl cation (C_2H_5^+) (**3**)*

It has long been known^{92,93} that this ion has a non-classical, bridged C_{2v} structure and that the classical C_s form is a saddle point on the potential energy surface of the C_2H_5^+ manifold⁹⁴ (Fig. 5).

The rewardingly coincident $\Delta_f H_m^\circ(\text{g})$ values for this ion, reported in Table 1, were obtained from three experimental sources: (1) the proton affinity of ethylene;^{43, 81} (2) the ionization energy of the ethyl radical;⁹⁵ (3) the PFI-PE spectrum of $\text{C}_2\text{H}_5\text{Br}$,⁹⁶ combined with the $\Delta_f H_m^\circ(\text{g})$ of the appropriate neutral^{26,97} species. $S_m^\circ(\text{g})$, as obtained from the experimental PA and GB values for C_2H_4 together with the experimental $S_m^\circ(\text{C}_2\text{H}_4)$, is presented in Table 1 together with the computational value.

*Propan-2-ylum ion, iso-propyl cation ($\text{iso-C}_3\text{H}_7^+$) (**4**)*

According to theoretical calculations and experimental evidence in solution,^{22,98,99} this species has a *chiral* structure with C_2 symmetry but very low methyl rotation barriers (Fig. 6). Cation **4** has been studied in solution by NMR^{100,101} but no data seem to be available for this ion in the solid state.

$\Delta_f H_m^\circ(\text{4})$ has been obtained experimentally from the dissociative ionization onset for the 2-propyl chloride, bromide and iodide PFI-PEPICO TOF.¹⁰² The experimental value of the PA of propene⁸¹ leads to a very close result. These data are summarized in Table 1. The reader is referred to Ref. 102 for an extremely careful discussion on the experimental and calculated values of $\Delta_f H_m^\circ(\text{4})$. High-level theoretical calculations using various methods,^{47,83,98,99} are also in good

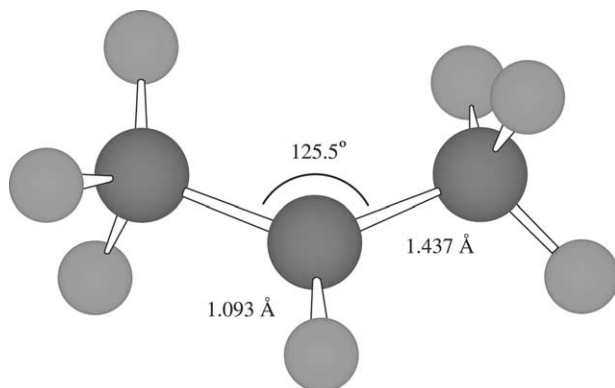


Fig. 6 Structure of propan-2-ylum ion, **4**, optimized at the MP2(full)/6-31G(d) level.

agreement with these results. They are presented in Table 1. $S^\circ_m(\mathbf{4})$ given in Table 1 is computed at the E3 level.⁴⁷

The classical structures of propan-1-ylum ion (1-propyl cation) are not minima on the potential energy surface of the $C_3H_7^+$ manifold.^{22,98} They are some 20 kcal mol⁻¹ above **4**, as determined computationally.⁹⁸ This result is in fair agreement with gas-phase photoionization experiments on the *n*-propyl radical by Schultz,¹⁰³ and Dyke and co-workers.¹⁰⁴ These structures are transition states involved in the hydrogen scrambling of **4** in superacidic media.^{22,105}

Butan-2-ylum ion, sec-butyl cation (sec-C₄H₉⁺) (5)

Experimental evidence (essentially IR and NMR data) in solution at low temperatures, summarized in Ref. 106, as well as high-level *ab initio* calculations¹⁰⁶ indicate that this ion exists as a mixture of structures **I** and **II**, of, respectively, C_2 and C_1 point group symmetries (Fig. 7).

The GB of *E*-C₄H₈ has been determined experimentally by ICR, using bracketing techniques.¹⁰⁷ We have carried out G2 calculations providing computed GB values for *E*-C₄H₈ and leading to structures **I** and **II**. These calculations show: (1) that the thermodynamic stabilities of both structures are extremely close and, more precisely, that a gaseous sample of *sec*-C₄H₉⁺ in thermal equilibrium at 298.15 K is very nearly a 1:1 mixture of isomers **I** and **II**; (2) that these computed GB values are in extremely good agreement with experiment. We have combined the experimental GB, $\Delta_f H^\circ_m$ and S°_m for *E*-C₄H₈ and the computed S°_m values for structures **I** and **II** to derive the corresponding values for $\Delta_f H^\circ_m(\mathbf{5})$ (Table 1). Arnett and co-workers^{108,109} used low-temperature calorimetry in superacids to determine the standard enthalpy change for the isomerization *sec*-C₄H₉⁺ \rightarrow *tert*-C₄H₉⁺. This datum, combined with $\Delta_f H^\circ_m(\textit{tert}\text{-C}_4\text{H}_9^+)$, provides an “apparent” value (assuming negligible differential solvation effects) of $\Delta_f H^\circ_m(\mathbf{5})$ quite consistent with the independent results reported above for the gas phase.

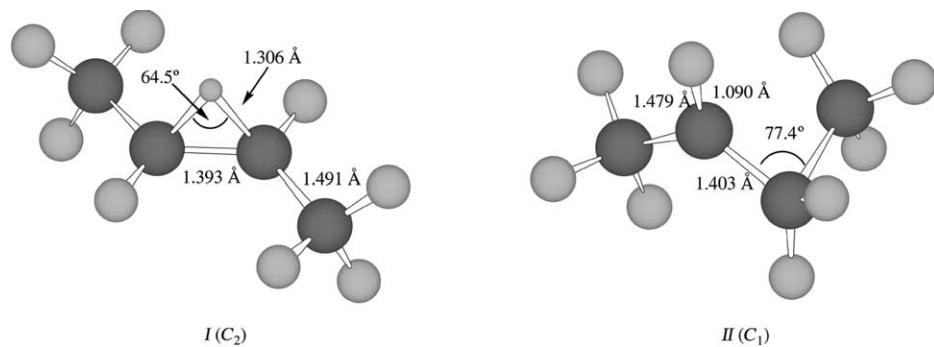


Fig. 7 Isomeric structures **I** and **II** of butan-2-ylum ion, **5**, optimized at the MP2(full)/6-31G(d) level.

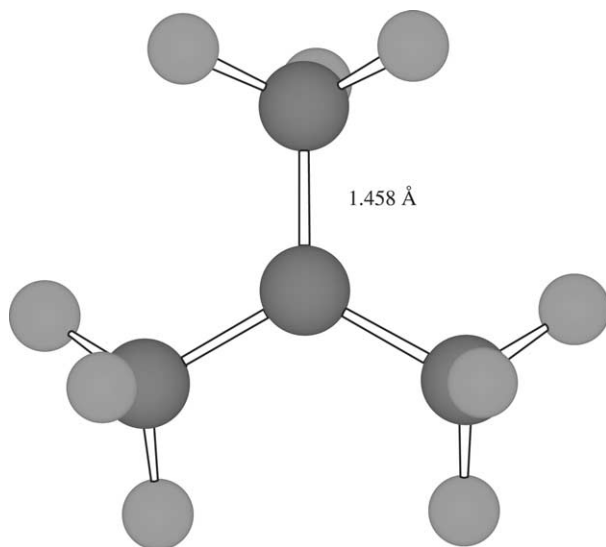


Fig. 8 Structure of 2-methylpropan-2-ylum ion, **6**, optimized at the MP2(full)/6-31G(d) level.

The primary cations $n\text{-C}_4\text{H}_9^+$ and $iso\text{-C}_4\text{H}_9^+$ are not on the minima on the PES of the C_4H_9^+ manifold.¹⁰⁶ The stability of these species can be estimated from vertical ionization potentials of appropriate substrates.¹¹⁰ The corresponding $\Delta_f H_m^\circ$ values are some 30 kcal mol^{-1} more positive than $\Delta_f H_m^\circ(tert\text{-C}_4\text{H}_9^+)$.

2-Methylpropan-2-ylum ion, *tert*-butyl cation ($tert\text{-C}_4\text{H}_9^+$) (**6**)

Solid state nutation NMR spectroscopy¹¹¹ and X-ray diffraction,¹¹² show that this ion has a trigonal structure with 1.46 and 2.51 Å for central-methyl and C–C methyl–methyl distances (Fig. 8).

Remarkably coincident experimental values for $\Delta_f H_m^\circ(\mathbf{6})$ can be obtained from: (1) PEPICO studies on *tert*-butyl iodide;¹¹³ (2) appearance energies for the formation of **6** from isobutane, neopentane and *tert*-butyl iodide (threshold photoionization mass spectrometry);¹¹⁴ (3) the PA of *iso*-butene.⁸¹ They are presented in Table 1, together with $S_m^\circ(\mathbf{6})$ determined from the experimental values of PA and GB(*iso*- C_4H_8),¹¹⁵ together with $\Delta_f H_m^\circ(iso\text{-C}_4\text{H}_8)$ and $S_m^\circ(iso\text{-C}_4\text{H}_8)$.

G2 values for the PA and GB of *iso*- C_4H_8 , particularly with entropies treated according to Ref. 47, lead to thermodynamic data in excellent agreement with experiment. Recent very high-level calculations¹¹⁶ on the *tert*-butyl radical also provide extremely consistent results. Our *ab initio* [MP2(full)/6-31G(d)] geometries are in excellent agreement with experimental data.

ALIPHATIC CARBOCATIONS WITH MORE THAN FOUR CARBON ATOMS

2-Methylbutan-2-ylum ion (tert-C₅H₁₁⁺) (7)

To our knowledge, there are no X-ray data on the structure of this ion. Its ¹³C NMR spectrum in solution has long been known.¹¹⁷

The experimental $\Delta_f H^\circ_m(7)$ and $S^\circ_m(7)$ values reported in Table 2 were obtained from the experimental standard enthalpy and Gibbs energy changes for the hydride exchange between ions **6** and **7** (reaction (21)) as determined by pulsed HPMS:^{118,119}



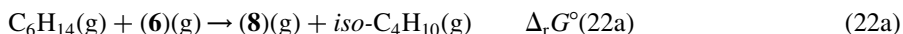
The structure of this ion, shown in Fig. 9, was fully optimized at the MP2(full)/6-31G(d) level (this work) and belongs to the C_s symmetry point group. Schleyer and co-workers¹²⁰ pointed out two important properties of this structure: (1) the lengthening of the C3–C4 bond to *ca.* 1.58 Å, indicative of hyperconjugation; (2) the reduction of the C4–C3–C2⁺ angle to 101.5°, showing distortion of the C–C hyperconjugating form toward bridging. This implies some “non-classical” character for **7**.

The computed ¹³C NMR shifts for this structure are in excellent agreement with experiment. This is not the case for other conformations, close in energy but not displaying this incipient bridging.¹²⁰

We have computed $\Delta_r G^\circ(21)$ and $\Delta_r H^\circ(21)$ at the G2(MP2) level. They are in excellent agreement with experiment and lead to $\Delta_f H^\circ_m(7)$ and $S^\circ_m(7)$ values, also given in Table 2.

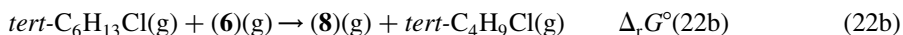
2-Methylpentan-2-ylum ion (tert-C₆H₁₃⁺) (8)

To our knowledge, no experimental structural data are available for this species. The experimental $\Delta_f H^\circ_m(8)$ and $S^\circ_m(8)$ were obtained from the experimental standard enthalpy and Gibbs energy changes for the hydride exchange between ions **6** and **8**, reaction (22a), as determined by pulsed HPMS:^{119,121}



Fully independent values of $\Delta_f H^\circ_m(8)$ and $S^\circ_m(8)$, also reported in Table 2, were obtained as follows:

(1) We applied the DPA technique to 2-chloro-2-methylpentane and to other tertiary alkyl chlorides.⁶⁸ These data lead to $\Delta_r G^\circ(22b)$:



Upon the appropriate leaving group corrections, this immediately provides $\Delta_r G^\circ(22a)$. This datum, corrected for the entropy terms, yields $\Delta_r H^\circ(22a)$, which in turn, upon combination with the experimental $\Delta_f H^\circ_m$ for 2-methylpentane, **6** and *iso*-C₄H₁₀(g) leads to a value of $\Delta_f H^\circ_m(8)$ in very good agreement with the results presented above.

(2) All the species involved in reaction (22a) were studied at the MP2/6-311G(d,p) level in Ref. 68; $\Delta_r H^\circ(22a)$ obtained from these calculations provides a value of $\Delta_f H^\circ_m(8)$ in satisfactory agreement with experiment.

Table 2 Thermodynamic data for selected aliphatic carbocations with five and more carbon atoms

Cations	$\Delta_f H^\circ_m(\text{g})^a$	$S^\circ_m(\text{g})^b$
2-Methylbutan-2-ylum (<i>tert</i> -C ₅ H ₁₁ ⁺) (7)	162.4 ± 2.0 ^c 164.1 ± 2.0 ^d	83.3 ± 2.0 ^c 85.2 ± 2.0 ^e
2-Methylpentan-2-ylum (<i>tert</i> -C ₆ H ₁₃ ⁺) (8)	156.2 ± 2.0 ^f 155.0 ± 3.0 ^h 154.3 ± 2.0 ^j	92.2 ± 2.0 ^g 91.1 ± 2.0 ⁱ
2,4-Dimethylpentan-2-ylum (C ₇ H ₁₅ ⁺) (9)	147.4 ± 2.1 ^k 146.7 ± 2.0 ^m	96.1 ± 2.0 ^l
2,4,4-Trimethylpentan-2-ylum (C ₈ H ₁₇ ⁺) (10)	139.8 ± 2.1 ⁿ 140.5 ± 2.1 ^p 139.2 ± 2.1 ^q	101.0 ± 2.0 ^o
3-Ethyl-5,5-dimethylhexan-3-ylum (C ₁₀ H ₂₁ ⁺) (11)	128.3 ± 2.1 ^r 129.0 ± 2.1 ^t 126.8 ± 2.0 ^u	113.2 ± 2.0 ^s
2,2,4,6,6-Pentamethylheptan-4-ylum (C ₁₂ H ₂₅ ⁺) (12)	112.0 ± 2.1 ^v 113.3 ± 2.1 ^x 110.8 ± 2.0 ^y	125.1 ± 2.0 ^w

^aIn kcal mol⁻¹.^bIn cal mol⁻¹ K⁻¹.^cFrom $\Delta_f H^\circ(21) = -2.6 \pm 1.0$ and $\Delta_f G^\circ(21) = -1.9 \pm 0.5$ kcal mol⁻¹, respectively; averages of data from Refs. 118 and 119. $\Delta_f H^\circ_m(\text{C}_5\text{H}_{12}) = -36.73 \pm 0.14$ kcal mol⁻¹ (Ref. 43) and $S^\circ(\text{C}_5\text{H}_{12})$, 82.2 cal mol⁻¹ K⁻¹.²⁹^dFrom $\Delta_f H^\circ(21) = -0.93 \pm 1.0$ kcal mol⁻¹ at the G2(MP2) level (this work).^eScaled HF/6-31G(d) value from the calculations in (d).^fFrom $\Delta_f H^\circ(22a) = -4.2 \pm 1.0$ and $\Delta_f G^\circ(22a) = -4.1 \pm 0.5$ kcal mol⁻¹, respectively; averages of data from Refs. 119 and 121. $\Delta_f H^\circ_m(\text{C}_6\text{H}_{14}) = -41.66 \pm 0.25$ kcal mol⁻¹ (Ref. 43) and $S^\circ(\text{C}_6\text{H}_{14}) = 91.1$ cal mol⁻¹ K⁻¹.²⁹^gFrom the data in (f).^hBased on $\Delta_f H^\circ(22a) = -5.4 \pm 2.8$ kcal mol⁻¹ from DPA experiments⁶⁸ treated as indicated in the text.ⁱScaled HF/6-31G(d) value from the calculations in Ref. 68.^jFrom the MP2/6-311G(d,p) value of $\Delta_f H^\circ(22a)$.⁶⁸^kDetermined from the DPA results for chlorides⁶⁸ with the appropriate leaving group and entropy corrections indicated in the text.^lScaled, computed HF/6-31G(d) value from data in Ref. 68.^mBased on the MP2/6-311G(d,p) data anchored, to the experimental $\Delta_f H^\circ_m[\text{C}_7\text{H}_{16}(\text{g})]$, -48.30 ± 0.23 kcal mol⁻¹.²⁶ⁿDetermined from the DPA results for chlorides⁶⁸ with the appropriate leaving group and entropy corrections indicated in the text.^oScaled, computed HF/6-31G(d) value from data in Ref. 68.^pAs in (n) but based on the DPA of the corresponding alcohol.^qBased on the MP2/6-311G(d,p) data anchored to the experimental $\Delta_f H^\circ_m[\text{C}_8\text{H}_{18}(\text{g})]$, -53.57 ± 0.32 kcal mol⁻¹.²⁶^rDetermined from the DPA results for chlorides⁶⁸ with the appropriate leaving group and entropy corrections indicated in the text.^sScaled, computed HF/6-31G(d) value from data in Ref. 68.

^fAs in (a) but based on the DPA of the corresponding alcohol.

^gBased on the MP2/6-311G(d,p) data anchored to the experimental $\Delta_f H^\circ_{\text{m}}[\text{C}_{10}\text{H}_{22}(\text{g})]$, $-62.72 \pm 0.50 \text{ kcal mol}^{-1}$.²⁸

^hDetermined from the DPA results for chlorides⁶⁸ with the appropriate leaving group and entropy corrections indicated in the text.

ⁱScaled, computed HF/6-31G(d) value from data in Ref. 68.

^xAs in (v) but based on the DPA of the corresponding alcohol.

^yBased on the MP2/6-311G(d,p)//MP2/6-31G(d) data anchored to the experimental $\Delta_f H^\circ_{\text{m}}[\text{C}_{12}\text{H}_{26}(\text{g})]$, $-75.43 \pm 0.50 \text{ kcal mol}^{-1}$.²⁸

Notice in Fig. 10 that the C3–C4 bond is elongated as in the case of **7**. This can also be taken as implying some contribution from hyperconjugation.¹²⁰

2,4-Dimethylpentan-2-ylum ($\text{C}_7\text{H}_{15}^+$) (**9**), *2,4,4-trimethylpentan-2-ylum* ($\text{C}_8\text{H}_{17}^+$) (**10**), *3-ethyl-5,5-dimethylhexan-3-ylum* ($\text{C}_{10}\text{H}_{21}^+$) (**11**) and *2,2,4,6,6-pentamethylheptan-4-ylum* ($\text{C}_{12}\text{H}_{25}^+$) (**12**) ions

To our knowledge, no experimental structural information is available for these species (Chart 1).

Experimental thermodynamic information on these ions was obtained by DPA using chlorides and alcohols as substrates.⁶⁸ Treatment of the experimental data by

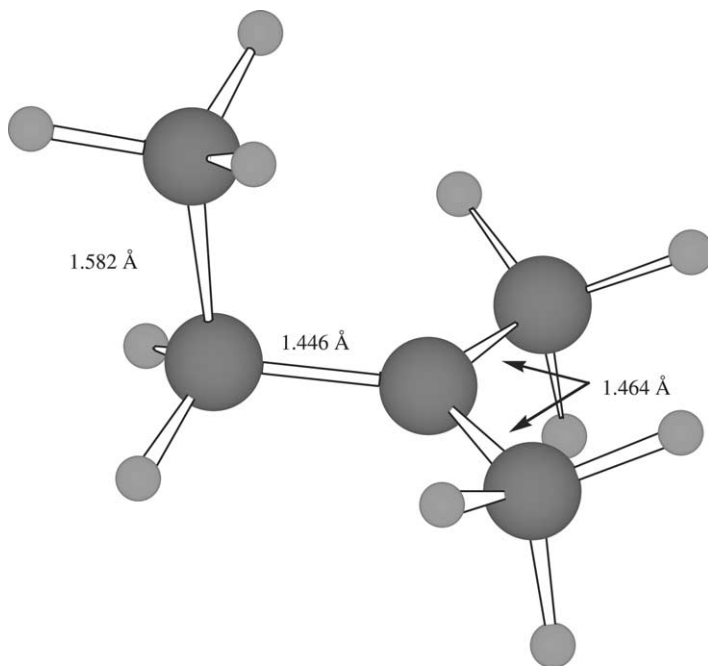


Fig. 9 Structure of 2-methylbutan-2-ylum ion, **7**, optimized at the MP2(full)/6-31G(d) level.

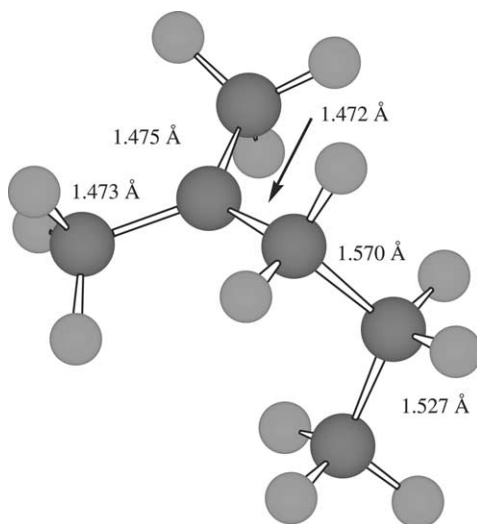


Fig. 10 Structure of 2-methylpentan-2-ylum ion, **8**, optimized at the MP2(full)/6-31G(d) level.

the methods indicated above led to the $\Delta_f H_m^\circ$ values summarized in Table 2. Relevant structural features of these ions, as determined by *ab initio* methods shall be reported in due course. Here, we notice that the experimental $\Delta_f H_m^\circ$ values are in good agreement with the MP2/6-311G(d,p) data, as shown in Table 2.

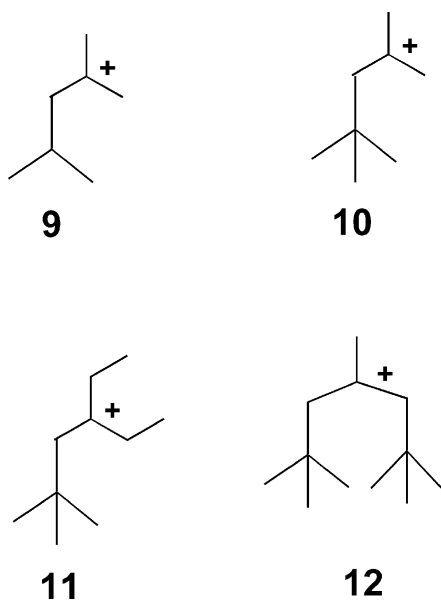


Chart 1

CYCLIC SPECIES WITHOUT FORMAL π SYSTEMS*Cyclopropylium ion* ($c\text{-C}_3\text{H}_5^+$) (**13**)

In principle, the species of C_{2v} symmetry,^{99,122} Fig. 11, can be formed in the gas phase by protonation of cyclopropene²¹ and by photoionization of the cyclopropyl radical.¹⁰⁴

These methods lead to rather different values of $\Delta_f H_m^\circ(\mathbf{13})$. Thus, using $\Delta_f H_m^\circ(c\text{-C}_3\text{H}_4) = 66.22 \pm 0.60 \text{ kcal mol}^{-1}$ (Ref. 27) and $\text{PA}(c\text{-C}_3\text{H}_4) = -195.6 \text{ kcal mol}^{-1}$, (Ref. 43) we get $\Delta_f H_m^\circ(\mathbf{13}) \approx 236.3 \text{ kcal mol}^{-1}$. Combining the ionization energy of the cyclopropyl radical, $8.18 \pm 0.03 \text{ eV}$,¹⁰⁴ with $\Delta_f H_m^\circ(c\text{-C}_3\text{H}_5) = 63.7 \pm 2.7 \text{ kcal mol}^{-1}$ based on the experimental ICR data from Ref. 123, we obtain $\Delta_f H_m^\circ(\mathbf{13}) \approx 252.7 \text{ kcal mol}^{-1}$.

High-level *ab initio* calculations fully rationalize these discrepancies. Thus, it has been shown that the cyclic C_{2v} structure is not a minimum on the potential energy surface of the $c\text{-C}_3\text{H}_5^+$ manifold.^{124,125} We have confirmed at the MP2(full)/6-311 + G(d,p) level that this is indeed the case. As indicated by Glukhovtsev *et al.*¹²² the cyclic C_{2v} structure appears as a shallow minimum at the HF/6-31G(d) level. We took advantage of this to estimate the PA of $c\text{-C}_3\text{H}_4$ at the standard G2 level. The value we obtain, $171.3 \text{ kcal mol}^{-1}$, puts $\Delta_f H_m^\circ(\mathbf{13})$ at about $260.6 \text{ kcal mol}^{-1}$. Notice that the meaning of the apparent $\text{PA}(c\text{-C}_3\text{H}_4)$ has been recently re-interpreted.¹²⁶

All these facts are perfectly consistent with solution chemistry results showing the essentially barrierless electrocyclic disrotatory ring opening of cyclopropyl cations

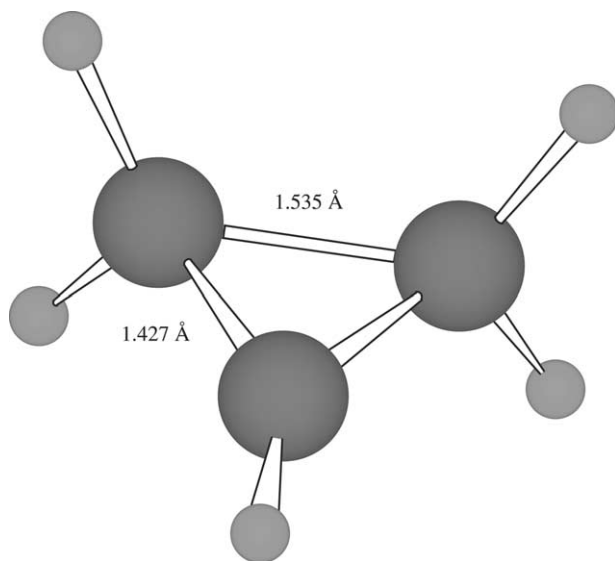


Fig. 11 Structure of cyclopropylium ion, **13**, optimized at the HF/6-31G(d) level. This structure is not a minimum at correlated levels.

to yield allylic cations in solvolytic processes,¹²⁷ this being a classical example of a pericyclic reaction.¹²⁸ To our knowledge, only a single-substituted cyclopropylium ion has been observed by NMR (in $\text{SbF}_5\text{--SO}_2\text{ClF}$ solution between -120 and -60°C), the 11-methyl-tricyclo[4.4.1.0^{1,6}]undec-11-yl cation.¹²⁹

Cyclobutylium ($c\text{-C}_4\text{H}_7^+$) (14) and cyclopropylmethylium ($c\text{-C}_3\text{H}_5\text{CH}_2^+$) (15) ions

Because of their relevance in physical organic chemistry a great deal of experimental information is available on these species, an excellent summary being given in Ref. 131. According to high-level calculations,^{130,131} **14** has a puckered structure (symmetrical, non-classical bicyclobutonium, C_s point group), as shown in Fig. 12.

It is known experimentally¹³⁰ that in solution at low temperature, **14** is in equilibrium with the bisected (C_s symmetry point group) **15**, (Fig. 13), and that the interconversion barrier is small (*ca.* 2 kcal mol⁻¹).

Notice that the bisected structure of **15** is taken to reflect the stabilizing interaction^{132–134} between the empty p orbital of the CH_2^+ moiety and the Walsh orbital^{135–139} of the cyclopropyl ring.

As regards the thermodynamic state functions for the equilibrating mixture of these two ions in the gas phase, we believe that the only piece of information available so far is the GB of cyclobutene.²⁶ This datum, combined with the experimental $S^\circ_{\text{m}}(c\text{-C}_4\text{H}_6)$ and the computed $S^\circ_{\text{m}}(\mathbf{14})$ (this work) leads to $\Delta_f H^\circ_{\text{m}}(\mathbf{14})$ (Table 3).

Our G2 calculations provide PA and GB values for $c\text{-C}_4\text{H}_6$ to yield **14** which, once combined with the experimental thermodynamic data for $c\text{-C}_4\text{H}_6$, lead to the

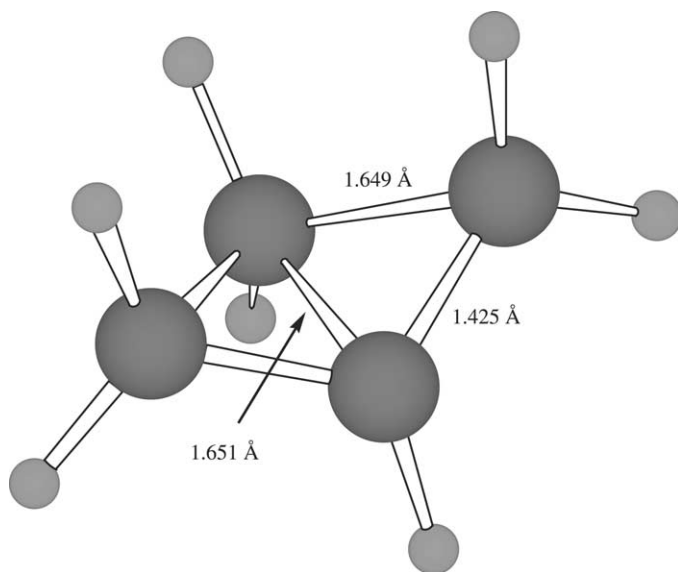


Fig. 12 Structure of cyclobutylium ion, **14**, optimized at the MP2(full)/6-31G(d) level.

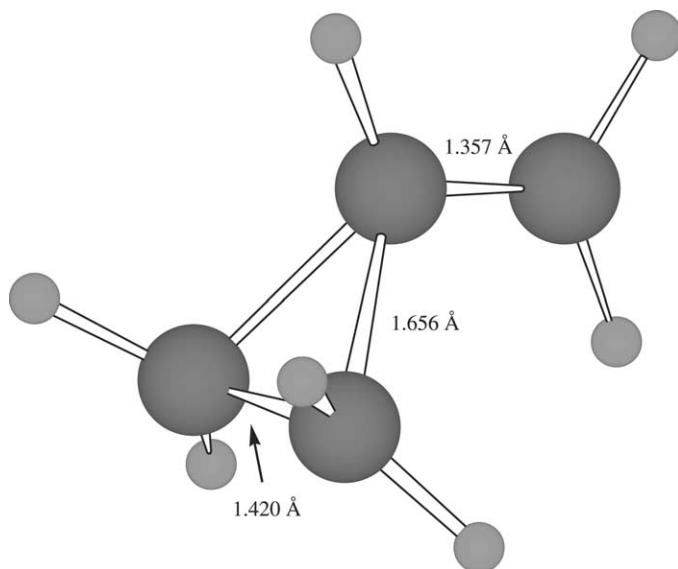


Fig. 13 Structure of cyclopropylmethylium ion, **15**, optimized at the MP2(full)/6-31G(d) level.

value of $\Delta_f H_m^\circ(\mathbf{14})$ reported in Table 3. As can be seen, the agreement with experiment is only moderately good.

High-level *ab initio* calculations^{130,131} have already indicated that species **14** and **15** have very close thermodynamic stabilities. Our own investigations show that, at the G2 level, $\Delta_f H^\circ(23)$ and $\Delta_f G^\circ(23)$ are, respectively, equal to -0.5 and $0.0 \text{ kcal mol}^{-1}$:



That $\Delta_f G_m^\circ(23) \approx 0 \text{ kcal mol}^{-1}$ is in remarkably good agreement with the results of solvolytic studies.^{130,140} This and $\Delta_f H_m^\circ(23) = -0.5 \text{ kcal mol}^{-1}$ imply that in solution at -132°C , an equilibrating mixture of these cations contains about 72 and 28%, respectively, of isomers **14** and **15**, in very fair agreement with experiment.¹³⁰

It has just been reported¹⁴¹ that two different C_4H_7^+ ions can be generated in the gas phase from cyclobutyl and cyclopropylcarbinyl chlorides. When sampled shortly (*ca.* 10^{-6} s) after their formation and in the absence of excitation, they display different patterns of reactivity, quite consistent with the structures given above for **14** and **15**.

Cyclopentylum ion (*c*- C_5H_9^+) (**16**)

This ion is known in solution at low temperature and has been studied in superacid media¹⁴² and even at 70 K in the solid state.¹⁴³

Table 3 Thermodynamic data for cyclic carbocations C4 and C5

Cations	$\Delta_f H_m^\circ(\text{g})^a$	$S_m^\circ(\text{g})^b$
Cyclobutylum, $c\text{-C}_4\text{H}_7^+$ (14)	216.3 \pm 2.2 ^c 212.2 \pm 2.2 ^{e,f} 212.0 \pm 2.3 ^{f,g}	67.6 \pm 2.0 ^d
Cyclopropylmethylum, $c\text{-C}_3\text{H}_5\text{CH}_2^+$ (15)	218.4 \pm 2.2 ^h 214.4 \pm 2.2 ^{f,i} 213.0 \pm 2.3 ^{f,k}	69.5 \pm 2.0 ^j
Cyclopentylum, $c\text{-C}_5\text{H}_9^+$ (16)	193.1 \pm 2.0 ^l 193.7 \pm 2.0 ^m 191.9 \pm 2.0 ^o	69.7 \pm 2.0 ⁿ

^aIn kcal mol⁻¹.^bIn cal mol⁻¹ K⁻¹.^cFrom the experimental GB($c\text{-C}_4\text{H}_6$), 180.1 kcal mol⁻¹ (Ref. 21), $\Delta_f H_m^\circ(c\text{-C}_4\text{H}_6) = 37.5 \pm 0.4$ kcal mol⁻¹ (Ref. 26) and $S_m^\circ(c\text{-C}_4\text{H}_6) = 62.6 \pm 2.0$ cal mol⁻¹ K⁻¹ (Ref. 30) and the computed [MP2(FC)/6-311G(d,p)], scaled $S_m^\circ(\textbf{14})$, 67.6 \pm 2.0 cal mol⁻¹ K⁻¹.^dComputed, scaled MP2(FC)/6-311G(d,p) value.^eFrom the computed PA($c\text{-C}_4\text{H}_6$) to yield **14**, 190.8 kcal mol⁻¹ and the experimental $\Delta_f H_m^\circ(c\text{-C}_4\text{H}_6)$.^fThese values seem more reliable than those based on the experimental GB($c\text{-C}_4\text{H}_6$).^gG2-computed value.^hFrom the experimental GB($c\text{-C}_4\text{H}_6$), $\Delta_f H_m^\circ(c\text{-C}_4\text{H}_6)$ and $S_m^\circ(c\text{-C}_4\text{H}_6)$, and the computed [MP2(FC)/6-311G(d,p)], scaled $S_m^\circ(\textbf{15})$, 69.5 \pm 2.0 cal mol⁻¹ K⁻¹ and assuming $\Delta_f G_m^\circ(\textbf{14}) = \Delta_f G_m^\circ(\textbf{15})$, on the basis of G2 calculations.ⁱFrom the G2-computed PA($c\text{-C}_4\text{H}_6$) to yield **15**, 190.3 kcal mol⁻¹ and the experimental $\Delta_f H_m^\circ(c\text{-C}_4\text{H}_6)$.^jComputed, scaled MP2(FC)/6-311G(d,p) value.^kG2-computed value.^lFrom the experimental $\Delta_f H_m^\circ(c\text{-C}_5\text{H}_8) = -18.36 \pm 0.36$ kcal mol⁻¹ (Ref. 26), $S_m^\circ(c\text{-C}_5\text{H}_8) = 69.2$ cal mol⁻¹ K⁻¹ (Ref. 30), $\Delta_f H_m^\circ(\textbf{24})$ and $\Delta_f G_m^\circ(\textbf{24})$ from Ref. 149 and the appropriate data for $iso\text{-C}_3\text{H}_7^+(\text{g})$ (Table 1).^mAs above, but using data from Refs. 117, 147 and 148.ⁿScaled, symmetry-corrected value from the calculations in (o).^oAs above, using our computed G2(MP2) values of $\Delta_f H_m^\circ(\textbf{24})$ and $\Delta_f G_m^\circ(\textbf{24})$.

¹H and ¹³C NMR spectra show **16** to have a highly fluxional structure, this being a consequence of very rapid 1,2-hydride shifts.^{144,145}

Its structure in the gas phase, as obtained at various correlated *ab initio* levels¹⁴⁶ is twisted (C_2 symmetry), as shown in Fig. 14. This is important because: (1) It shows, as shown in Fig. 14, that the C(1)–C(2)–H_a and C(1)–C(2)–H_c angles are quite different and the C–H_a bond lengths are relatively large, as they fit to partial hydrogen bonding and to a hyperconjugative effect. The same holds for the hydrogens bound to C(5); (2) this structure is able to account for the experimental ¹³C NMR spectra of **16** in solution and in the solid state.

Experimental standard thermodynamic state functions for this ion in the gas phase can be obtained from the following sources: the GB of cyclopentene, an ICR

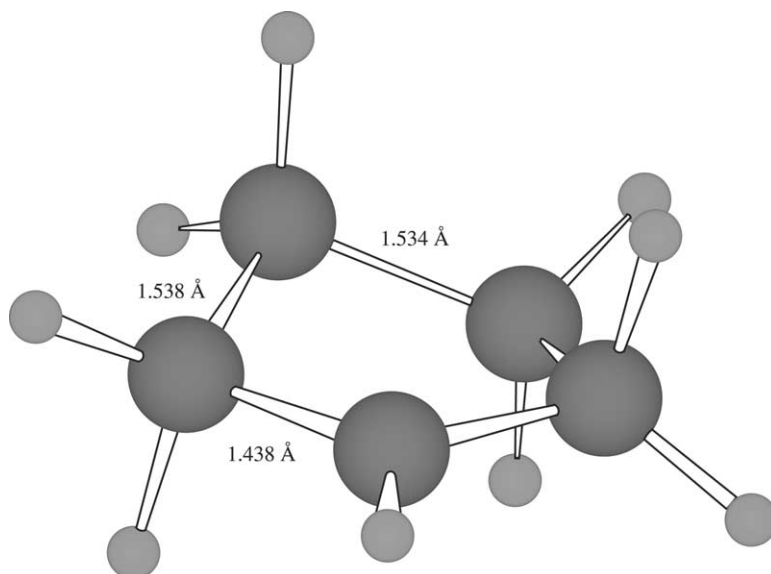
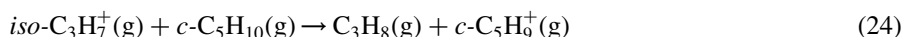


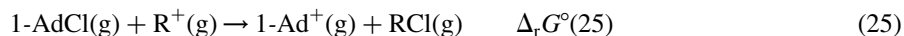
Fig. 14 Structure of cyclopentylum ion, **16**, optimized at the MP2(full)/6-31G(d) level.

bracketing value from Ref. 107 and the standard Gibbs energy change and enthalpy for reaction (24)^{121,148,149} as determined by HPMS:



These thermodynamic data are collected in Table 3, together with the results of our G2(MP2) calculations. The agreement is reasonable.

For the purposes of linking the present results to those obtained by the DPA technique, the standard Gibbs energy change for reaction (25), a chloride ion exchange between a carbocation (R^+) (**16** in this case) and 1-adamantyl cation (1-Ad⁺), is necessary. We obtained this datum by combining the experimental $\Delta_r G^\circ(24)$ with the computed value of the standard Gibbs energy change for the chlorine exchange between 1-adamantyl chloride and cyclopentane, no experimental data being available for cyclopentyl chloride. The result is reported in Table 4:



Notice that in some cases, *tert*-C₄H₉Cl has been used instead of 1-AdCl as a reference.

CYCLOPROPYL-SUBSTITUTED CARBOCATIONS

The stabilizing interactions between the empty p orbital in the methyl cation and the Walsh orbital of cyclopropane reported in the case of **15** are also present in other cognate ions. Some examples are as follows.

Table 4 Standard Gibbs energy changes for reaction (25), $\Delta_r G_m^\circ(25)$

Cation	$\Delta_r G_m^\circ(25)$
Methylum (CH_3^+) (1)	-77.4 ± 2.8^a
Propan-2-ylum (<i>iso</i> - C_3H_7^+) (4)	-22.7 ± 3.0^a
Butan-2-ylum (<i>sec</i> - C_4H_9^+) (5)	-18.9 ± 3.0^a
2-Methylpropan-2-ylum (<i>tert</i> - C_4H_9^+) (6)	-6.0 ± 1.0^b
2-Methylpentan-2-ylum (<i>tert</i> - $\text{C}_6\text{H}_{13}^+$) (8)	-1.1 ± 2.8^c
2,4-Dimethylpentan-2-ylum ($\text{C}_7\text{H}_{15}^+$) (9)	1.9 ± 2.8^c
2,4,4-Trimethylpentan-2-ylum ($\text{C}_8\text{H}_{17}^+$) (10)	4.9 ± 2.8^c
3-Ethyl-5,5-dimethylhexan-3-ylum ($\text{C}_{10}\text{H}_{21}^+$) (11)	7.6 ± 2.8^c
2,2,4,6,6-Pentamethylheptan-4-ylum ($\text{C}_{12}\text{H}_{25}^+$) (12)	13.3 ± 2.8^c
Cyclopropylmethylum (<i>c</i> - $\text{C}_3\text{H}_5\text{-CH}_2^+$) (15)	-7.1 ± 2.0^d
Cyclopentylum (<i>c</i> - C_5H_9^+) (16)	-13.6 ± 2.5^a
1-Cyclopropylethan-1-ylum (<i>c</i> - $\text{C}_3\text{H}_5\text{-CHCH}_3^+$) (17)	2.0 ± 2.0^d
2-Cyclopropylpropan-2-ylum (<i>c</i> - $\text{C}_3\text{H}_5\text{-C(CH}_3)_2^+$) (18)	14.2 ± 2.0^d
Dicyclopropylmethylum [<i>(c</i> - $\text{C}_3\text{H}_5)_2\text{-CH}^+$] (19)	12.0 ± 2.0^d
1,1-Dicyclopropylethan-1-ylum [<i>(c</i> - $\text{C}_3\text{H}_5)_2\text{CCH}_3^+$] (20)	22.1 ± 2.0^d
Tricyclopropylmethylum [<i>(c</i> - $\text{C}_3\text{H}_5)_3\text{C}^+$] (21)	29.0 ± 3.0^c
Norbornan-1-ylum (1-Nb $^+$) ($\text{C}_7\text{H}_{11}^+$) (22)	-27.3 ± 2.8^c
Norbornan-2-ylum (2-Nb $^+$) ($\text{C}_7\text{H}_{11}^+$) (23)	-3.0 ± 1.0^b
Norbornan-7-ylum (7-Nb $^+$) ($\text{C}_7\text{H}_{11}^+$) (24)	-22.2 ± 2.8^c
Bicyclo[2.2.2]octan-1-ylum ($\text{C}_8\text{H}_{13}^+$) (26)	-7.4 ± 2.8^c
Noradamantan-3-ylum ($\text{C}_{10}\text{H}_{13}^+$) (27)	-17.4 ± 2.8^c
Adamantan-1-ylum ($\text{C}_{10}\text{H}_{13}^+$) (28)	0.00 (by definition)
Adamantan-2-ylum ($\text{C}_{10}\text{H}_{13}^+$) (29)	-7.6 ± 2.8^c (-11.3 ± 3.0) ^e
Bicyclo[3.3.2]decan-1-ylum ($\text{C}_{10}\text{H}_{17}^+$) (30)	10.4 ± 3.3^c
Homoadamantan-3-ylum ($\text{C}_{11}\text{H}_{17}^+$) (31)	4.7 ± 2.8^c
Homoadamantan-4-ylum ($\text{C}_{11}\text{H}_{17}^+$) (32)	-0.9 ± 3.0^c
Bicyclo[3.3.3]undecan-1-ylum ($\text{C}_{11}\text{H}_{17}^+$) (33)	13.2 ± 2.8^c
[1]Diadamantan-1-ylum ($\text{C}_{19}\text{H}_{27}^+$) (34)	16.7 ± 2.8^c
Cyclopropenylium (C_3H_3^+) (38)	5.2 ± 2.0^c
1,2-Dipropylcyclopropenylium [<i>c</i> - $\text{C}_3\text{H(C}_3\text{H}_7)_2^+$] (40)	32.3 ± 3.4^c
Tripropylcyclopropenylium [<i>c</i> - $\text{C}_3(\text{C}_3\text{H}_7)_3^+$] (41)	41.5 ± 3.4^c
Norbornen-7-ylum (C_7H_9^+) (43)	1.3 ± 2.8^c
Norbornadien-7-ylum (C_7H_7^+) (44)	6.9 ± 2.8^c
Cycloheptatrienylium (Tropylium) (C_7H_7^+) (45)	29.8 ± 2.0^d (32.3 ± 3.4) ^c
Benzylum (C_7H_7^+) (46)	-5.8 ± 2.0^b
4-Nitrobenzylum (4- $\text{NO}_2\text{-C}_6\text{H}_4\text{-CH}_2^+$)	-17.2 ± 2.0^b
4-Methoxybenzylum (4- $\text{MeO-C}_6\text{H}_4\text{-CH}_2^+$)	7.7 ± 2.0^b
1-Phenylethan-1-ylum (C_8H_9^+) (47)	1.7 ± 2.0^b
2-[4-Methoxyphenyl]propan-2-ylum [4- $\text{MeO-C}_6\text{H}_5\text{C(CH}_3)_2^+$]	16.7 ± 2.0^b
2-[3-Nitrophenyl]propan-2-ylum [3- $\text{NO}_2\text{-C}_6\text{H}_5\text{C(CH}_3)_2^+$]	-3.2 ± 2.0^b
2-Phenylpropan-2-ylum ($\text{C}_9\text{H}_{11}^+$) (48)	6.4 ± 1.0^b
Diphenylmethanylium ($\text{C}_{13}\text{H}_{11}^+$) (49)	13.4 ± 3.0^f
1,1-Diphenylethan-1-ylum ($\text{C}_{14}\text{H}_{13}^+$) (50)	23.5 ± 3.0^f
Triphenylmethanylium ($\text{C}_{19}\text{H}_{15}^+$) (51)	28.4 ± 3.0^f

All values in kcal mol^{-1} . Specific details for each ion are given in the text.

^aFrom the $\Delta_f H_m^\circ(\text{g})$ and $S_m^\circ(\text{g})$ values for ions, as reported in the various tables. Whenever a choice was possible, the most accurate value was used. Data for 1-AdCl and **28** are from Ref. 64. Data for other neutral species are either experimental or computed as indicated in the text.

^bDirect experimental value (equilibrium techniques).

^cFrom DPA experiments and, when necessary, the appropriate leaving group correction for chloride, (see text).

^dCalculated at the G2(MP2) level.

^eWith leaving group correction for OTs.

^fFrom the computed $\Delta_f H_m^\circ(g)$ ¹⁵⁵ and the leaving group correction for chloride.

1-Cyclopropylethan-1-ylum ion ($c\text{-C}_3\text{H}_5\text{CHCH}_3^+$) (**17**)

Compound **17** has been obtained at low temperature in superacid media.¹⁵⁰ Both its ^1H and ^{13}C NMR spectra are known.¹⁵¹

NMR evidence indicates that it has a bisected structure (C_s symmetry), the most stable isomer having the methyl group in position *trans* relative to the ring (see Fig. 15).

$\Delta_f H_m^\circ(\textbf{17})$ as reported in Table 5 was obtained from the experimental standard enthalpy of formation³¹ and the PA of vinylcyclopropane as given in Ref. 43, based on (ICR) GB data from Taft's group.

G2(MP2) calculations (this work) provide thermodynamic data also reported there. Interestingly, the computed $\Delta_f H_m^\circ$ value for gaseous vinylcyclopropane is in excellent agreement with the literature data.^{31,35} The structure for the *trans* form of the ion at the MP2(full)/6-31G(d) level is portrayed in Fig. 15. $\Delta_r G_m^\circ(25)$ is given in Table 4.

2-Cyclopropylpropan-2-ylum ion ($c\text{-C}_3\text{H}_5\text{C}(\text{CH}_3)_2^+$) (**18**)

This ion has been generated in solution at low temperature in superacid medium.¹⁵⁰ The ^1H and ^{13}C NMR spectra of this and cognate ions are reported and discussed in Refs. 151 and 152.

Theoretical calculations, such as those performed in this work, lead to the structure presented in Fig. 16, in which the plane defined by the carbons of the 2-propyl moiety is a perpendicular bisector of the cyclopropyl ring, as in the case of the 1-cyclopropylethyl cation. This is an important result, in full agreement with the NMR spectrum of the ion. Furthermore, rotation around the C(1)–C(α) bond involves a barrier of *ca.* 13.7 kcal mol^{–1}.¹⁵³ These structural features, as well as those presented by **15** and **17**, are consequences of the stabilizing interaction between the strained C–C bonds of the cyclopropane moiety and the formally empty p orbital of the alkyl moiety.^{135–140}

The value of $\Delta_f H_m^\circ(\textbf{18})$ given in Table 5 was obtained from the experimental PA of 2-propenylcyclopropane. This value is that recommended in Ref. 43, based on scaled data from Taft's group and Ref. 21. We also report $\Delta_f H_m^\circ[c\text{-C}_3\text{H}_5\text{C}(\text{CH}_3)_2]^+$ from our G2(MP2) calculations. $\Delta_r G_m^\circ(25)$ is given in Table 4.

Dicyclopolylmethylum ion [$(c\text{-C}_3\text{H}_5)_2\text{CH}^+$] (**19**)

The ^1H NMR spectrum of **19** in solution in superacid media was reported in 1970.¹⁵³ As far as we know, its structure in the solid state is not yet available. The X-ray

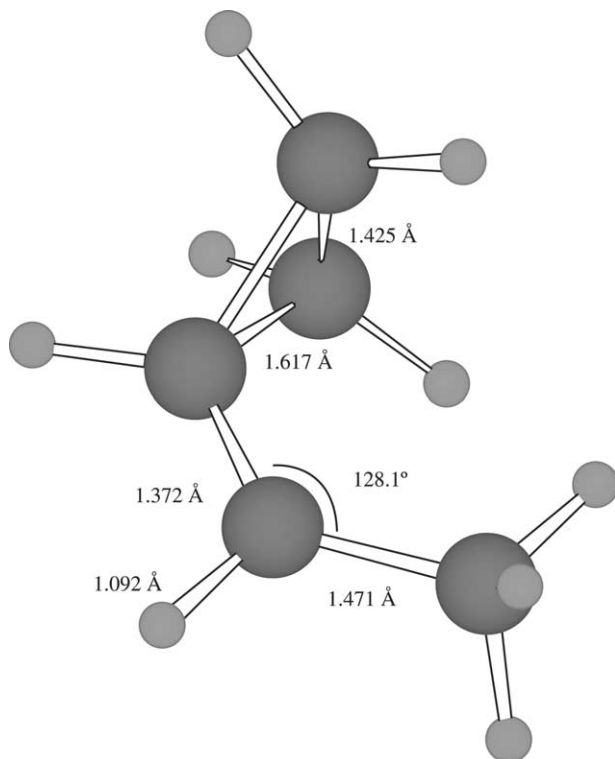


Fig. 15 Structure of 1-cyclopropylethan-1-ylum ion, **17**, optimized at the MP2(full)/6-31G(d) level.

structure of the hexafluoroantimonate of hydroxydicyclopropylmethylium is known, however,¹⁵⁴ and shows that both rings adopt an essentially “bisected” structure. The structure of **19**, optimized at the MP2(full)/6-31G(d) level, has C_2 symmetry (Fig. 17) and also shows this feature.

No thermodynamic data seem to be available for this species in the gas phase. The data reported in Table 5 were obtained computationally at the MP4(SDQ)/6-31G(d)//MP2(full)/6-31G(d) level.¹⁵⁵ The computed $\Delta_r G^\circ(25)$ is given in Table 4.

1,1-Dicyclopropylethan-1-ylum ion $[(c\text{-C}_3\text{H}_5)_2\text{CCH}_3^+]$ (**20**)

We are not aware of experimental structural data on this species. The structure we present here (Fig. 18) is that optimized at the MP2(full)/6-31G(d) level and has a C_s symmetry clearly showing the bisected positions of the cyclopropyl rings.

The value of $\Delta_f H^\circ_m[(c\text{-C}_3\text{H}_5)_2\text{CCH}_3^+]$ given in Table 5 was obtained from the experimental PA of $[(c\text{-C}_3\text{H}_5)_2\text{C}=\text{CH}_2]$ and the computed (this work) $\Delta_f H^\circ_m(\text{g})$ for

Table 5 Thermodynamic data for selected cyclopropyl-containing carbocations

Cations	$\Delta_f H_m^\circ(\text{g})^a$	$S_m^\circ(\text{g})^b$
1-Cyclopropylethan-1-ylum ($c\text{-C}_3\text{H}_5\text{CHCH}_3^+$) (17)	201.1 \pm 2.1 ^c 197.6 \pm 2.1 ^{e,f} 194.5 \pm 2.1 ^{f,g}	77.6 \pm 2.0 ^d
2-Cyclopropylpropan-2-ylum ($c\text{-C}_3\text{H}_5\text{C}(\text{CH}_3)_2^+$) (18)	178.8 \pm 2.1 ^h 180.0 \pm 2.1 ⁱ 181.2 \pm 2.1 ^k	84.6 \pm 2.0 ^j
Dicyclopropylmethylium ($(c\text{-C}_3\text{H}_5)_2\text{CH}^+$) (19)	217.5 \pm 2.0 ^l	82.0 \pm 2.0 ^m
1,1-Dicyclopropylethan-1-ylum ($(c\text{-C}_3\text{H}_5)_2\text{CCH}_3^+$) (20)	199.3 \pm 4.0 ⁿ	92.9 \pm 2.0 ^o
Tricyclopropylmethylium ($(c\text{-C}_3\text{H}_5)_3\text{C}^+$) (21)	232.0 \pm 4.0 ^p	97.8 \pm 2.0 ^q

^aIn kcal mol⁻¹.^bIn cal mol⁻¹ K⁻¹.^cFrom the experimental PA of vinylcyclopropane,⁴³ 195.1 \pm 2.0 kcal mol⁻¹ and $\Delta_f H_m^\circ(c\text{-C}_3\text{H}_5\text{CHCH}_2) = 30.40 \pm 0.30$ kcal mol⁻¹.³⁵^dScaled HF/6-31G(d) value from this work.^eFrom the computed (G2MP2) PA of $c\text{-C}_3\text{H}_5\text{CHCH}_2$, 199.0 kcal mol⁻¹ and the experimental $\Delta_f H_m^\circ(c\text{-C}_3\text{H}_5\text{CHCH}_2)$.^fValues more reliable than those based on the experimental PA of vinylcyclopropane. See Ref. 126.^gFrom the computed $\Delta_f H_m^\circ$ for the hydride exchange between **17** and **4** together with the experimental value of $\Delta_f H_m^\circ(c\text{-C}_3\text{H}_5\text{CH}_2\text{CH}_3)$.^hFrom the experimental PA of 2-propenylcyclopropane,⁴³ 208.3 \pm 2.0 kcal mol⁻¹ and $\Delta_f H_m^\circ(c\text{-C}_3\text{H}_5\text{CCH}_2\text{CH}_3) = 21.4 \pm 0.5$ kcal mol⁻¹ from Refs. 31 and 35.ⁱFrom the computed (G2MP2) PA of $c\text{-C}_3\text{H}_5\text{CCH}_2\text{CH}_3$, 207.0 kcal mol⁻¹ and the experimental and $\Delta_f H_m^\circ(c\text{-C}_3\text{H}_5\text{CCH}_2\text{CH}_3)$.^jScaled HF/6-31G(d) value extracted from the G2(MP2) calculation.^kFrom the computed [G2(MP2)] $\Delta_f H_m^\circ$ for the hydride exchange between 2-cyclopropyl-2-propyl cation and *tert*-butyl cation and the experimental $\Delta_f H_m^\circ$ values for all the other species.^lComputed at the G2(MP2) level (this work).^mScaled HF/6-31G(d) value from this work.ⁿFrom the experimental PA[$(c\text{-C}_3\text{H}_5)_2\text{C}=\text{CH}_2$], 216.2 kcal mol⁻¹⁴³ and the computed $\Delta_f H_m^\circ[(c\text{-C}_3\text{H}_5)_2\text{C}=\text{CH}_2]$ (see text).^oScaled, symmetry-corrected HF/6-31G(d) value from this work.^pFrom the DPA onset of tricyclopropylcarbinol and the computed $\Delta_f H_m^\circ[(c\text{-C}_3\text{H}_5)_3\text{CH}]$ (this work).^qScaled, symmetry-corrected HF/6-31G(d) value from this work.

this species. The former is taken from Ref. 43 and is based on experimental ICR data from Taft's group and Ref. 21. $\Delta_f H_m^\circ[(c\text{-C}_3\text{H}_5)_2\text{C}=\text{CH}_2]$ was estimated through the combination of experimental $\Delta_f H_m^\circ$ (vinylcyclopropane, g) and the enthalpy of the isodesmic reaction (26) computed at the MP4(SDQ)/6-31G(d)//MP2(full)/6-31G(d) level.¹⁵⁶ It is difficult to assess the uncertainty of this value, but it might reach some 2–3 kcal mol⁻¹. The computed $\Delta_f H_m^\circ$ (25) is given in Table 4:



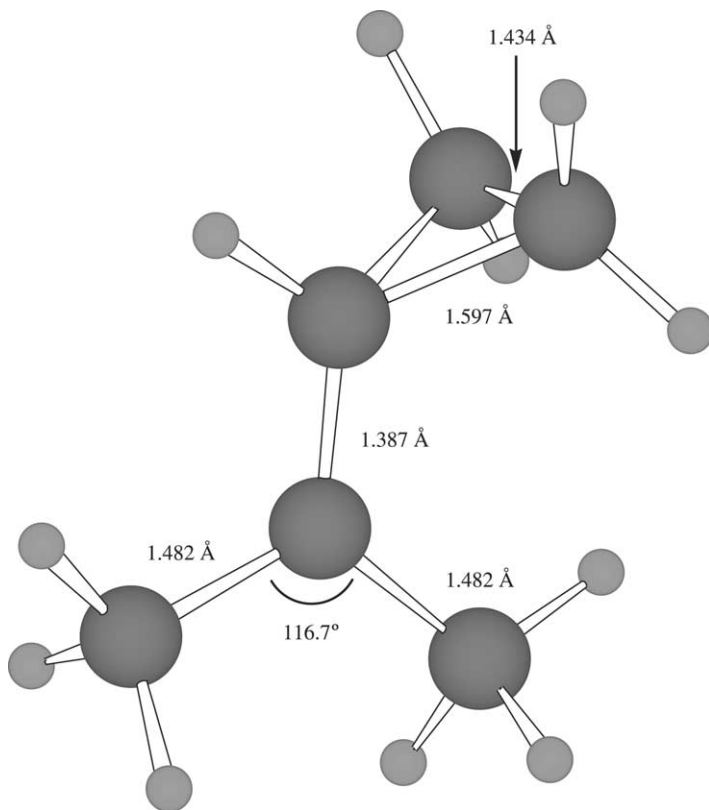


Fig. 16 Structure of 2-cyclopropylpropan-2-ylum ion, **18**, optimized at the MP2(full)/6-31G(d) level.

Tricyclopropylmethylium ion [(*c*-C₃H₅)₃C⁺] (**21**)

This is a remarkably stable ion, already observed in 1955.¹⁵⁷ Its first ¹H NMR spectrum (in H₂SO₄ at room temperature!) was reported in 1962¹⁵⁸ and so were a little later, the spectra of a variety of cyclopropyl carbocations in superacid media.¹⁵⁹ Its ¹³C spectrum has been carefully analyzed.^{160,161}

The structure computed at the MP2(full)/6-31G(d) level (this work) and portrayed in Fig. 19 is propeller-shaped and has *C*_{3*h*} symmetry. It obviously minimizes internal repulsions between the rings while allowing for maximal simultaneous overlap between the empty p orbital of the central carbon and the Walsh orbitals of the rings. This situation is to be compared to that prevailing in the trityl cation, which is much less favorable.

No thermodynamic data for this ion in the gas phase seem to be available so far. We have carried out DPA studies of tricyclopropyl carbinol and its methyl ether. This provides Δ_f*H*^o_m(**21**). Unfortunately, the associated uncertainty is somewhat

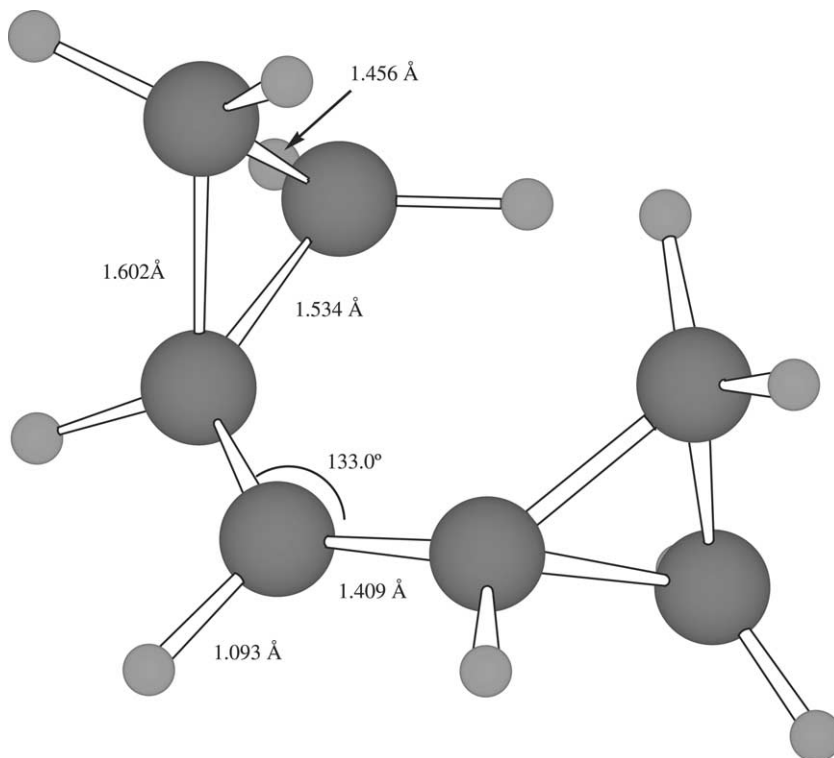


Fig. 17 Structure of dicyclopropylmethyl cation, **19**, optimized at the MP2(full)/6-31G(d) level.

large because of the unavailability of experimental enthalpies of formation for tricyclopropylmethane and other relevant species. As in the previous case, no G2-type calculations could be performed on these species because of their size. Instead, the enthalpy of the isodesmic reaction (27) was computed at the MP4(SDQ)/6-31G(d)/MP2(full)/6-31G(d) level¹⁵⁶ and combined with the experimental value of $\Delta_f H^\circ_m(c\text{-C}_3\text{H}_5\text{CH}_3)$ to obtain $\Delta_f H^\circ_m[(c\text{-C}_3\text{H}_5)_3\text{CH}]$. The computed $\Delta_f G^\circ_m(25)$ is given in Table 4:



SECONDARY AND TERTIARY CARBOCATIONS DERIVED FROM CAGE HYDROCARBONS

Norboman-1-ylum ion (1-Nb⁺) (C₇H₁₁⁺) (**22**)

To our knowledge, this highly strained ion^{57,58,162,163} has not been observed in solution or in the solid state. It is known that in solution under stable ion

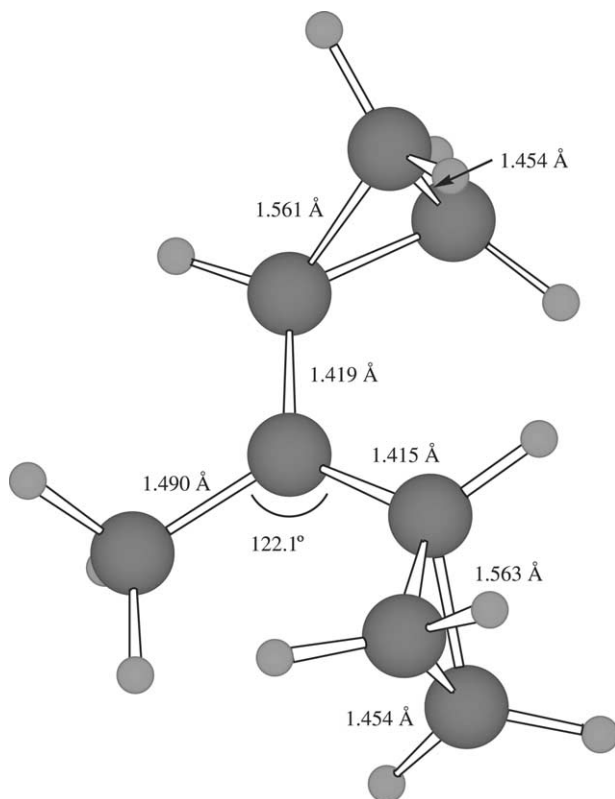


Fig. 18 Structure of 1,1-dicyclopropylethan-1-ylum ion, **20**, optimized at the MP2(full)/6-31G(d) level.

conditions, it is not observed and it rearranges to yield a 2-norbornyl cation.¹⁶⁴ No high-level *ab initio* studies seem to have been published by other workers on this species. Figure 20 portrays its optimized structure at the MP2(full)/6-31G(d) level.

The stability of this ion was experimentally estimated by DPA^{57,58} using as substrates the corresponding chloride and bromide. The experimental $\Delta_r G^\circ(25)$, is reported in Table 4.

The DPA onset for 1-NbCl, subject to leaving group and entropy corrections similar to those used for **6**, led to the value of $\Delta_r H^\circ(22)$ reported in Table 6. This table also presents $\Delta_r H^\circ(22)$ obtained at the G2(MP2) level.

Norbornan-2-ylum ion (2-Nb⁺) (C₇H₁₁⁺) (**23**)

Few species have raised so much interest and for such a long period of time as **23**.^{165–170}

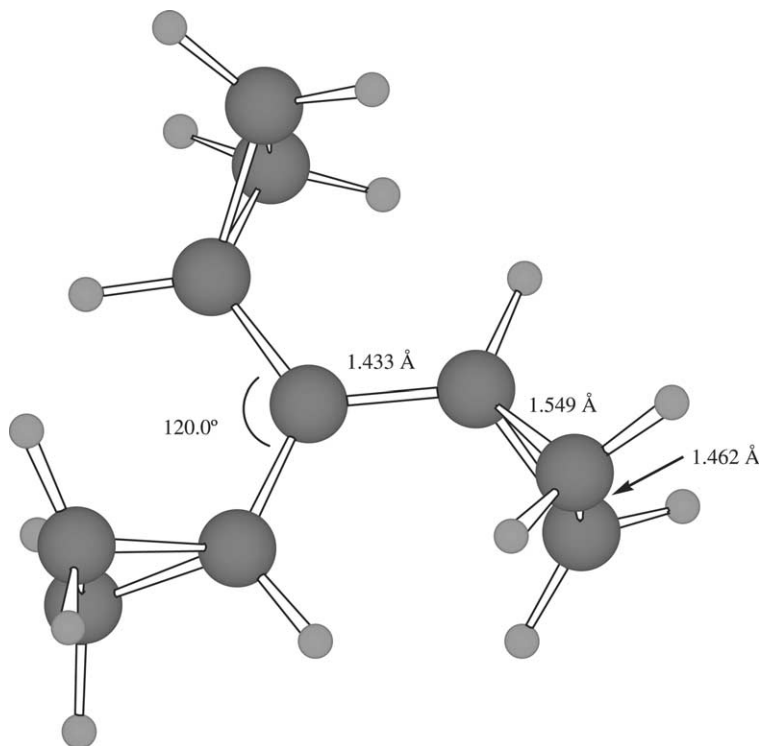


Fig. 19 Structure of tricyclopropylmethyl cation, **21**, optimized at the MP2(full)/6-31G(d) level.

^{13}C and ^1H NMR spectra of this ion in superacid media at low temperatures,^{171,172} as well as in the solid state at 5 K,¹⁷³ strongly indicate that this ion has the “non-classical” structure depicted in Fig. 21.

The IR¹⁷⁴ and ESCA¹⁷⁵ spectra of this ion at low temperature also support this contention.

High-level *ab initio* calculations in Ref. 176 and references therein agree with these results. Our own G2(MP2) data, based on this non-classical structure, lead to energetic values in excellent agreement with experiment (see Table 6). It is interesting that these concepts have been challenged very recently.¹⁷⁷

The experimental thermodynamic state functions presented in Table 6 have been obtained from the following sources: (1) the averaged, selected experimental values of PA and GB for norbornene;⁴³ (2) the experimental HPMS standard Gibbs energy change for the hydride exchange between *tert*-butyl and 2-norbornyl cations;¹⁴⁹ (3) the standard Gibbs energy change for the chloride exchange between *tert*-butyl and 2-norbornyl cations as determined from DPA results^{57,58} (see Table 4) and the appropriate leaving group and entropy corrections. All these results are extremely self-consistent.

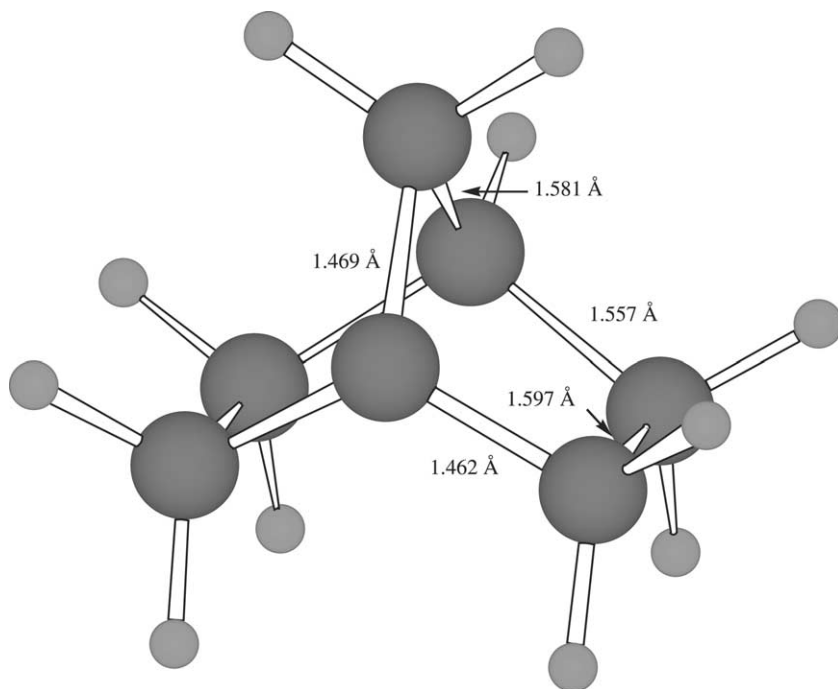


Fig. 20 Structure of norbornan-1-ylum ion, **22**, optimized at the MP2(full)/6-31G(d) level.

*Norbornan-7-ylum ion (7-Nb⁺) (C₇H₁₁⁺) (**24**)*

To our knowledge, this ion has not been observed in solution in superacid media although its IR spectrum, using the SbF₅ matrix technique at very low temperatures, has been obtained from various precursors, including 7-norbornyl chloride.^{178,179} These experiments, together with high-level *ab initio* calculations,^{179,180} indicate that **24** has the non-classical (C₁ symmetry) structure portrayed in Fig. 22.

7-Norbornyl chloride was subject to DPA treatment in the gas phase.¹⁸¹ As in the cases discussed above, its reaction onset was used to estimate $\Delta_r G^\circ(25)$ (Table 4). Also, applying the same kind of leaving group and entropy corrections, the value of $\Delta_f H_m^\circ(24)$ reported in Table 6 was obtained. $\Delta_f H_m^\circ(24)$ computed at the G2(MP2) level is also given in Table 6.

*Cubylum ion (C₈H₇⁺) (**25**)*

The stability of this ion (Chart 2) was obtained by direct bromide exchange with 3-noradamantyl cation, prepared in turn by DPA of the 3-bromonoradamantane.^{57,58} For the sake of consistency with the treatment in Refs. 57 and 58, $\Delta_f H_m^\circ(25)$ reported in Table 6 was anchored to that for the 1-adamantyl cation, using for the

Table 6 Thermodynamic data for secondary and tertiary carbocations derived from cage hydrocarbons

Cations	$\Delta_f H_m^\circ(\text{g})^a$	$S_m^\circ(\text{g})^b$
Norbornan-1-ylum ($\text{C}_7\text{H}_{11}^+$) (22)	208.7 ± 3.1^c 204.8 ± 2.0^e	77.0 ± 2.0^d
Norbornan-2-ylum ($\text{C}_7\text{H}_{11}^+$) (23)	186.1 ± 2.1^f 185.8 ± 2.1^g 186.3 ± 3.0^i 187.1 ± 2.0^j	78.8 ± 2.0^h
Norbornan-7-ylum ($\text{C}_7\text{H}_{11}^+$) (24)	205.6 ± 3.0^k 203.2 ± 2.0^l	76.4 ± 2.0^m
Cubylum (C_8H_7^+) (25)	360.2 ± 3.8^n 358.9 ± 3.2^o	85.6 ± 2.0^p
Bicyclo[2.2.2]octan-1-ylum ($\text{C}_8\text{H}_{13}^+$) (26)	174.2 ± 3.0^q 176.1 ± 3.0^r	78.7 ± 2.0^s
Adamantan-1-ylum ($\text{C}_{10}\text{H}_{15}^+$) (28)	162.6 ± 3.0^t 164.1 ± 3.2^u 162.9 ± 3.2^v 160.7 ± 3.7^x	81.07 ± 2.0^w
Adamantan-2-ylum ($\text{C}_{10}\text{H}_{15}^+$) (29)	171 ± 3^y 171.9 ± 1.1^z 172.1 ± 1.1^{ab}	84.45 ± 2.0^{aa}
Bicyclo[3.3.2]decan-1-ylum ($\text{C}_{10}\text{H}_{17}^+$) (30)	160.5 ± 3.5^{ac} 161.6 ± 3.0^{ad}	85.3 ± 2.0^{ae}
Bicyclo[3.3.3]undecan-1-ylum ($\text{C}_{11}\text{H}_{19}^+$) (33)	161.7 ± 3.0^{af} 160.2 ± 3.0^{ag}	86.6 ± 2.0^{ah}

^aIn kcal mol⁻¹.^bIn cal mol⁻¹ K⁻¹.^cFrom the DPA results on 1-NbCl and *tert*-BuCl with the computed leaving group and entropy corrections^{57,58} and the $\Delta_f H_m^\circ$ values for *tert*-C₄H₉Cl and *iso*-C₄H₁₀, respectively, -42.99 ± 0.50 and -32.25 kcal mol⁻¹.²⁶ $\Delta_f H_m^\circ(\mathbf{6})$ is from Table 1.^dScaled value at the HF/6-31G* level.^eG2(MP2) computed value (this work).^fFrom the averaged, selected experimental values of PA and GB for norbornene⁴³ and the experimental $\Delta_f H_m^\circ(\text{C}_7\text{H}_{10})$, 19.7 ± 0.50 kcal mol⁻¹ (Ref. 26) and $S^\circ(\text{C}_7\text{H}_{10}) = 74.3 \pm 2.0$ cal mol⁻¹ K⁻¹ (Walsh, R. and Wells, J. M. (1976) *J. Chem. Thermodyn.* 8, 55).^gFrom the experimental HPMS¹⁴⁹ standard Gibbs energy change for the hydride exchange between *tert*-butyl and 2-norbornyl cations with scaled entropy corrections for all species from our G2(MP2) calculations.^hScaled value at the HF/6-31G* level.ⁱFrom the standard Gibbs energy change for the chloride exchange between *tert*-butyl and 2-norbornyl cations as determined from DPA results^{57,58} and the appropriate leaving group and entropy corrections, the latter as in (g).^jAs in (f) but using the computed [G2(MP2)] PA and GB of norbornene.

^kFrom the standard Gibbs energy change for the chloride exchange between *tert*-butyl and 7-norbornyl cations as determined from DPA results¹⁸¹ with the appropriate leaving group corrections (at the MP2(full)/6-31G(d) level). Entropy corrections are scaled, values at the HF/6-31G(d) level. Ancillary experimental data for the other species are from Tables 1 and 3. $\Delta_f H_m^\circ(\text{norbornane}) = 13.30 \pm 0.50 \text{ kcal mol}^{-1}$.²⁶

^lG2(MP2) value.

^mThe value of $S^\circ(\mathbf{24})$ is a scaled MP2(FU)/6-31G(d) value from this work.

ⁿExperimental value obtained as indicated in the text. Leaving group correction at the HF/6-31G(d) level. $\Delta_f H_m^\circ(\text{adamantane}) = -32.0 \pm 0.50 \text{ kcal mol}^{-1}$,²⁶ $\Delta_f H_m^\circ(\text{cubane}) = 148.7 \pm 1.0 \text{ kcal mol}^{-1}$,²⁶ $\Delta_f H_m^\circ(1\text{-adamantyl}) = -162.0 \pm 2.0 \text{ kcal mol}^{-1}$.⁶⁴

^oComputed at the MP2/6-311G(d,p) level. Anchored to experimental data as indicated in the text.

^pSymmetry-corrected HF/6-31G(d) value.⁵⁷

^qFrom the standard Gibbs energy change for the chloride exchange between *tert*-butyl and bicyclo[2.2.2]octyl cations as determined from DPA results⁵⁷ and the appropriate leaving group corrections (at the HF/6-31G(d) level). Entropy corrections at the HF/6-31G(d) level. Ancillary experimental data for the other species are from Tables 1 and 3.

^rComputed values at the MP2/6-311G(d,p) level for the hydride exchange between *tert*-butyl and bicyclo[2.2.2]octyl cations and anchored to the experimental data for *tert*-butyl cation and *iso*-butane. Entropy corrections at the HF/6-31G(d) level.

^sSymmetry-corrected HF/6-31G(d) value.⁵⁷

^tFrom HPMS data¹⁸⁶ for hydride exchange between *tert*-Bu⁺ and 1-Ad⁺ together with data from Ref. 26 for the neutral species.

^uFrom the same source, for the homologous chloride anion exchange, together with $\Delta_f H_m^\circ(\text{tert-C}_4\text{H}_9\text{Cl}) = 42.99 \pm 0.50 \text{ kcal mol}^{-1}$ (Ref. 26) and $\Delta_f H_m^\circ(1\text{-AdCl}) = -42.45 \pm 0.60 \text{ kcal mol}^{-1}$.⁶⁴

^vFrom the DPA and FT ICR equilibrium study of the same process with the entropy corrections (scaled, symmetry-corrected HF/6-31G(d) values) from Ref. 64.

^wScaled, symmetry-corrected HF/6-31G(d) value from Ref. 64.

^xAverage of the G2(MP2) calculations for hydride and chloride exchanges, anchored to the experimental $\Delta_f H_m^\circ(\text{g})$ values for the neutral species.

^yFrom Ref. 189.

^zFrom Ref. 190 and ancillary data from Ref. 192.

^{aa}Computed [HF/6-31G(d)], scaled value.

^{ab}G2(MP2) value anchored to experimental data for *iso*-C₃H₇⁺ (Table 1) and *iso*-C₃H₇ (Ref. 26), see Ref. 192.

^{ac}From the standard Gibbs energy change for the chloride or hydroxyl exchanges between *tert*-butyl and bicyclo[3.3.2]decyl cations as determined from DPA results⁵⁷ and the appropriate leaving group corrections [at the HF/6-31G(d) level]. Entropy corrections are symmetry-corrected values at the HF/6-31G(d) level. Ancillary experimental data for the other species are from Tables 1 and 3. $\Delta_f H_m^\circ(\text{g})$ for bicyclo[3.3.2]decane is $-25.3 \pm 0.50 \text{ kcal mol}^{-1}$.²⁶

^{ad}Computed values at the MP2/6-311G(d,p) level for the hydride exchange between *tert*-butyl and bicyclo[3.3.2]decyl cations and anchored to the experimental data for *tert*-butyl cation and *iso*-butane. Entropy values are symmetry-corrected at the HF/6-31G(d) level.

^{ae}Computed [HF/6-31G(d)] value.

^{af}From the averaged standard Gibbs energy changes for the chloride or hydroxyl exchanges between *tert*-butyl and bicyclo[3.3.3]undecyl cations as determined from DPA results⁵⁷ and the appropriate leaving group corrections [at the HF/6-31G(d) level].⁵⁷ Entropy corrections are symmetry-corrected values at the HF/6-31G(d) level. Ancillary experimental data for the other species are from Tables 1 and 3. $\Delta_f H_m^\circ(\text{g})$ for bicyclo[3.3.3]undecane is $-21.2 \pm 0.50 \text{ kcal mol}^{-1}$.²⁶

^{ag}Computed values at the MP2/6-311G(d,p) level for the hydride exchange between *tert*-butyl and bicyclo[3.3.3]undecyl cations and anchored to the experimental data for *tert*-butyl cation and *iso*-butane. Entropy values are symmetry-corrected at the HF/6-31G(d) level.

^{ah}Computed [HF/6-31G(d)] value.

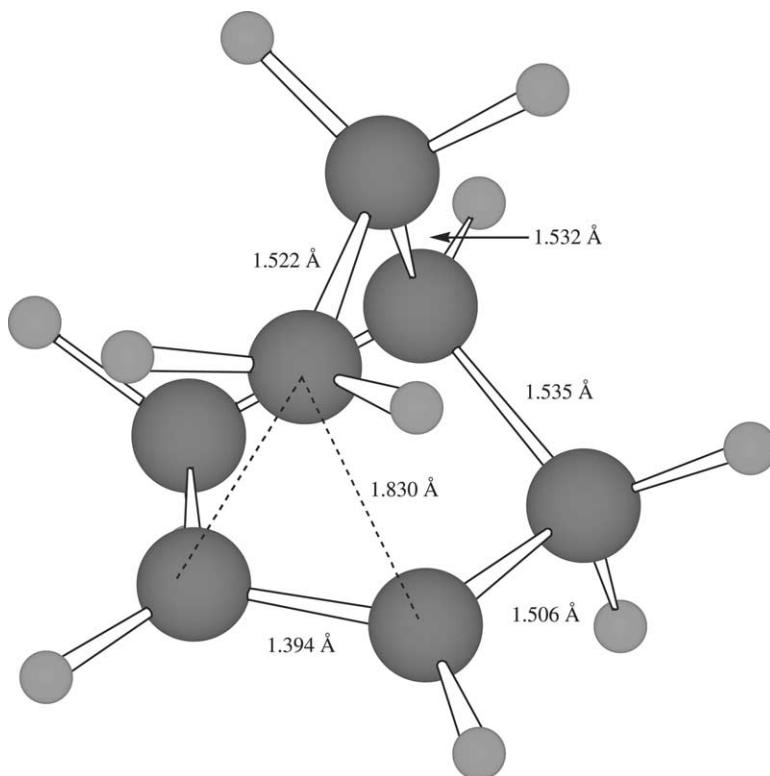


Fig. 21 Structure of norbornan-2-ylum ion, **23**, optimized at the MP2(full)/6-31G(d) level.

latter $\Delta_f H^\circ_m = 162.0 \pm 2.0 \text{ kcal mol}^{-1}$.⁶⁴ We also report the results computed at the MP2/6-311G(d,p) level.^{57,58}

*Bicyclo[2.2.2]octan-1-ylum ion ($\text{C}_8\text{H}_{13}^+$) (**26**)*

$\Delta_f H^\circ_m(\mathbf{26})$ (see Chart 2) presented in Table 6 is based on the DPA study of the 1-chlorobicyclo[2.2.2]octane⁵⁷ (see also Table 4). These results were shown to be in excellent agreement with those obtained from the corresponding bromide.⁵⁸ Experimental data were treated exactly as in the case of **25**. Computational results at the MP2/6-311G(d,p) level are also given in Table 6.

*Noradamantan-3-ylum ion ($\text{C}_{10}\text{H}_{13}^+$) (**27**)*

The $\Delta_r G^\circ(25)$ value given in Table 4 was obtained from the DPA study of 3-noradamantyl bromide with the appropriate leaving group corrections^{57,58} (see Chart 2).

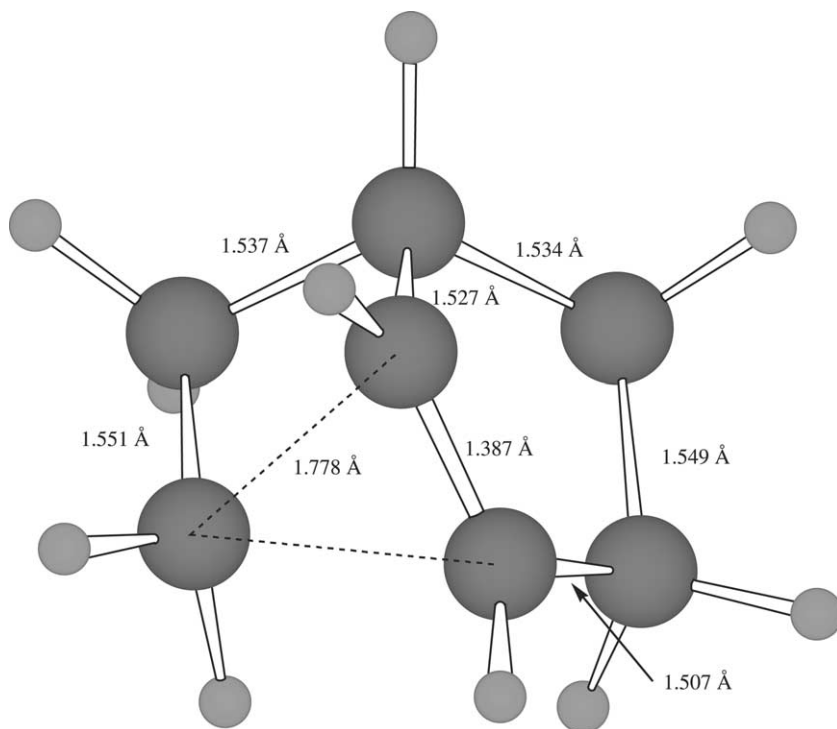


Fig. 22 Structure of norbornan-7-ylum ion, **24**, optimized at the MP2(full)/6-31G(d) level.

*Adamantan-1-ylum ion ($C_{10}H_{15}^+$) (**28**)*

This ion (see [Chart 2](#)) is of both historical and chemical importance. It was one of the first tertiary carbocations to be identified in solution in superacid media,¹⁸² studied by 1H and ^{13}C NMR in solution,¹⁸³ prepared as a stable solid salt,¹⁸⁴ and characterized by its IR spectrum in cryogenic SbF_5 matrices.¹⁸⁵ It was amongst the first ions to be studied by ICR through halide exchange reactions^{50,186} and also the first tertiary carbocation to undergo a systematic treatment by means of DPA.⁵⁴

$\Delta_f H_m^\circ(\mathbf{28})$, presented in [Table 6](#), is based on the most recent HPMS and FT ICR studies by hydride and halide exchanges^{58,60,187} (see [Table 4](#)). These results have been shown to be quite consistent with the G2(MP2) studies of both kinds of processes.⁶⁴ The value of $\Delta_f H_m^\circ(\mathbf{28})$ used here is $162.0 \pm 2.0 \text{ kcal mol}^{-1}$, simultaneously consistent with these experimental and computational data.

*Adamantan-2-ylum ion ($C_{10}H_{15}^+$) (**29**)*

As far as we know, this ion ([Chart 2](#)) has not been observed in solution or in the solid state. It has, however, been studied in the gas phase¹⁸⁶ and computationally at the MP2/6-31G(d)//6-31G(d) + ZPVE6-31G(d) level.¹⁸⁸

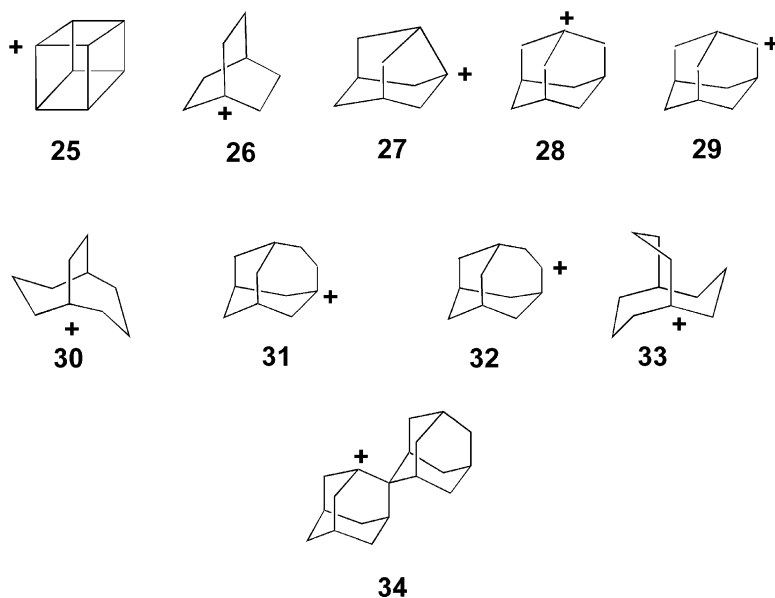


Chart 2

Thermodynamic experimental data for this ion comes from three sources: (1) its appearance energy from a variety of precursors;¹⁸⁹ (2) the adiabatic ionization energy of the 2-adamantyl radical;¹⁹⁰ (3) the DPA study of 2-adamantyl chloride and 2-adamantyl alcohol.¹⁹¹

On the basis of a G2(MP2) study of 1- and 2-adamantyl radicals and cations,¹⁹² the results by Aubry *et al.*¹⁸⁹ and Kruppa and Beauchamp¹⁹⁰ seem quite consistent,¹⁹¹ they are also in very good agreement with DPA studies of 2-adamantanol and 2-adamantyl chloride. The results are summarized in Table 6 (see also Table 4).

A value for $\Delta_f H_m^\circ(29)$ of $171.9 \pm 2.0 \text{ kcal mol}^{-1}$ is simultaneously consistent with these experimental and computational data.

Bicyclo[3.3.2]decan-1-ylum ion (C₁₁H₁₇⁺) (30)

The thermodynamic data for this ion presented in Table 6 were obtained from the DPA study of the corresponding alcohol and chloride.^{57,58} The average $\Delta_r G^\circ(25)$ is given in Table 4. Leaving group and entropy corrections were applied as in previous cases. Values obtained at the MP2/6-311G(d,p) level are reported in Table 4.

Homoadamantan-3-ylum ion (C₁₁H₁₇⁺) (31)

This ion (see Chart 2) was obtained from the DPA of the corresponding chloride and alcohol.^{57,58} The value of $\Delta_r G^\circ(25)$ given in Table 4 is the average of both results (with the appropriate leaving group correction).

Homoadamantan-4-ylum ion ($C_{11}H_{17}^+$) (**32**)

This ion ([Chart 2](#)) was obtained from the DPA of the corresponding chloride.¹⁹³ The experimental $\Delta_f G^\circ(25)$ value is given in [Table 4](#).

Bicyclo[3.3.3]undecan-1-ylum ion ($C_{10}H_{17}^+$) (**33**)

This ion was obtained from the DPA of the corresponding chloride and alcohol.^{57,58} The value of $\Delta_f G^\circ(25)$ given in [Table 4](#) is the average of both highly consistent results (with the appropriate leaving group correction). $\Delta_f H_m^\circ$ (**33**) derived therefrom is given in [Table 6](#) together with the results obtained at the MP2/6-311G(d,p) level.

Diadamantan-1-ylum ion ($C_{19}H_{27}^+$) (**34**)

This ion was obtained from the DPA of the corresponding chloride and alcohol.⁵⁸ The value of $\Delta_f G^\circ(25)$ given in [Table 4](#) is the average of both highly consistent results. Because of the size of the system, leaving group corrections were computed at the AM1 level.

CARBENIUM IONS WITH FORMAL π SYSTEMS*Vinylium ion* ($C_2H_3^+$) (**35**)

Experimental values for the standard enthalpy of formation of this ion, as reported in [Table 7](#), are in fair agreement. They originate in: (1) the proton affinity of acetylene¹⁹⁴ obtained in SIFT experiments; and (2) the adiabatic ionization energy of the vinyl radical¹⁹⁵ combined with its standard enthalpy of formation.²⁵

We have obtained $\Delta_f H_m^\circ(g)$ values for $C_2H_3^+$ by combining the standard enthalpy of protonation of acetylene as computed at the G2 level (this work) with the experimental $\Delta_f H_m^\circ(C_2H_2)$. Also used was the computed (G2) ionization energy of vinyl radical together with the experimental value of $\Delta_f H_m^\circ(C_2H_3)$ to obtain $\Delta_f H_m^\circ(C_2H_3^+)$. These values are presented in [Table 7](#). (see also Ref. 196).

Experimental spectroscopic studies in the millimeter wavelength region^{3,197,198} provided rotational constants and the inertial defect for this ion. These data show that the ground state of this species is planar and has a non-classical C_{2v} structure (**1**, [Fig. 23](#)). Near-IR studies of $C_2H_3^+$ led to results^{199,200} also in agreement with this non-classical structure. Furthermore, the splitting of the spectral lines was interpreted in terms of the tunneling of protons between the unequivalent axial and apical positions. This tunneling takes place through the classical structure **2** ([Fig. 23](#)). From the most recent work,¹⁹⁸ the difference in stability between these structures has been estimated at 4.7 kcal mol⁻¹.

The computed difference in standard enthalpies of formation between structures **1** and **2** amounts to 4.3 kcal mol⁻¹. High-level structural studies²⁰¹ reveal a small upward tilting (0.3°) of the axial hydrogens with respect to the internuclear C–C

Table 7 Thermodynamic data for non-aromatic carbocations with formal π bonds

Cations	$\Delta_f H_m^\circ(\text{g})^a$	$S_m^\circ(\text{g})^b$
Vinylum (C_2H_3^+) (35)	266.6 ± 3.2^c	52.4 ± 2.0^e
	269.9 ± 1.9^d	
	265.7 ± 2.5^f	
	266.8 ± 2.0^g	
2-Propargylium (C_3H_3^+) (36)	280.8 ± 1.1^h	59.3 ± 2.0^i
	279.6 ± 2.0^j	
2-Propenylum, allyl (C_3H_5^+) (37)	228.9 ± 0.6^k	60.4 ± 2.0^m
	226.0 ± 2.0^l	
	228.7 ± 2.0^n	

^aIn kcal mol⁻¹.^bIn cal mol⁻¹ K⁻¹.^cFrom the experimental PA(C_2H_2), 153.3 ± 3.2 kcal mol⁻¹ (Ref. 194) and $\Delta_f H_m^\circ(\text{C}_2\text{H}_2)$, 54.190 kcal mol⁻¹.²⁶^dFrom the adiabatic ionization energy of vinyl radical, 8.59 ± 0.03 eV (Ref. 195) and $\Delta_f H_m^\circ(\text{C}_2\text{H}_3) = 71.5 \pm 1.5$ kcal mol⁻¹.²⁵ See also Berkowitz, J., Ellison, G. B. and Gutman, D. (1994) *J. Phys. Chem.* 98, 2744 for a detailed discussion of the matter.^eSymmetry-corrected, scaled value at the HF/6-31G(d) level (this work).^fFrom the G2-computed ionization energy of vinyl radical (194.1 kcal mol⁻¹ at 0 K) and the experimental $\Delta_f H_m^\circ(\text{C}_2\text{H}_3)$ (this work).^gFrom the G2-computed PA(C_2H_2) (this work) (153.1 kcal mol⁻¹) and the experimental $\Delta_f H_m^\circ(\text{C}_2\text{H}_2)$.^hFrom the ionization energy of the propargyl radical²⁰⁷ and $\Delta_f H_m^\circ(\text{C}_3\text{H}_3) = 81.0 \pm 1.0$ kcal mol⁻¹ from Ref. 25. Thermal corrections from this work.ⁱScaled, corrected HF/6-31G(d) value from this work.^jThis work, using the computed (G2) ionization energy of C_3H_3 (8.673 eV)²⁰⁷ and $\Delta_f H_m^\circ(\text{C}_3\text{H}_3) = 81.0 \pm 1.0$ kcal mol⁻¹.²⁵ Thermal corrections from this work.^kFrom Ref. 212.^lFrom the experimental $\Delta_f H_m^\circ(\text{g})$ of allene, 45.6 ± 0.2 kcal mol⁻¹ (Ref. 27) and its experimental PA, 185.3 kcal mol⁻¹.¹⁹¹^mHF/6-31G(d) value from this work, scaled and symmetry corrected.ⁿThis work, using the experimental $\Delta_f H_m^\circ(\text{g})$ for allene and its G2-calculated PA (184.0 kcal mol⁻¹).

axis. Theory and computation on vinyl cations have been reviewed.²⁰² Studies on medium effects on acetylene and vinyl cation have been reported recently.²⁰³

Ab initio molecular dynamics^{204,205} calculations performed on vinyl cation confirm that the ground-state structure of C_2H_3^+ is best described as a quasi-planar bridged structure broadened significantly by anisotropic delocalization of the protons due to zero point motion.

2-Propargylium ion (C_3H_3^+) (**36**)

To our knowledge, no direct experimental spectroscopic data are available for the propargyl cation. Very large scale *ab initio* calculations have been carried out on both this ion and on the propargyl radical.²⁰⁶ They lead to vibrational frequencies for the latter in excellent agreement with experiment and to an adiabatic ionization

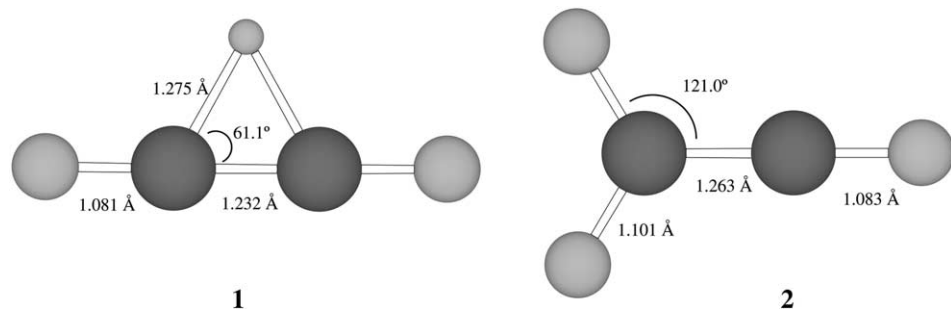


Fig. 23 Structure of vinyl cation, **35**, optimized at the MP2(full)/6-31G(d) level. Structure **1** is the absolute minimum. Structure **2** is a transition state.

potential for this radical (8.650 eV) pleasantly close to the experimental value (8.673 eV).^{207,208} $\Delta_f H^\circ_m(\mathbf{36})$ (Table 7) can be obtained experimentally from the standard enthalpy of formation of the propargyl radical²⁵ and the zero kinetic energy photoelectron spectrum (ZEKE) of this species.²⁰⁷

Recent calculations at the CBS-Q level⁹⁹ as well as our present G2 computations lead to values of $\Delta_f H^\circ_m(\mathbf{36})$ in excellent agreement with experiment (Table 7). They all confirm the C_{2v} symmetry of **36** (Fig. 24).

2-Propenylium ion, allyl cation ($C_3H_5^+$) (**37**)

According to careful *ab initio* calculations, this species is planar and has a C_{2v} symmetry (Fig. 25).^{209,210} According to Ref. 210, this planarity seems to be enforced by the σ framework although the contribution from the π conjugation is also relevant.

Based on the adiabatic ionization energy of the allyl radical as determined by Houle and Beauchamp²¹¹ and on its own work, the Boulder group²¹² determined a value of $\Delta_f H^\circ_m(\mathbf{37})$ in remarkable agreement with that obtained much earlier by Lossing²¹³ by means of appearance energies. $\Delta_f H^\circ_m(\mathbf{37})$ can also be derived from the experimental GB of allene (upon appropriate correction of entropy effects; see Table 7) obtained by ICR, using a bracketing technique.²¹⁴ $\Delta_f H^\circ_m(\mathbf{37})$ computed at the CBS-Q level⁹⁹ is in very nice agreement with the datum from Ref. 212. So is our own G2 result (see Table 7).

TWO-ELECTRON AROMATIC AND HOMOAROMATIC IONS

Cyclopropenylium ion ($C_3H_3^+$) (**38**)

This species, an “archetypal aromatic cation”¹²² has a planar, fully symmetrical structure (D_{3h} symmetry point group) (Fig. 26) as confirmed by the systematic

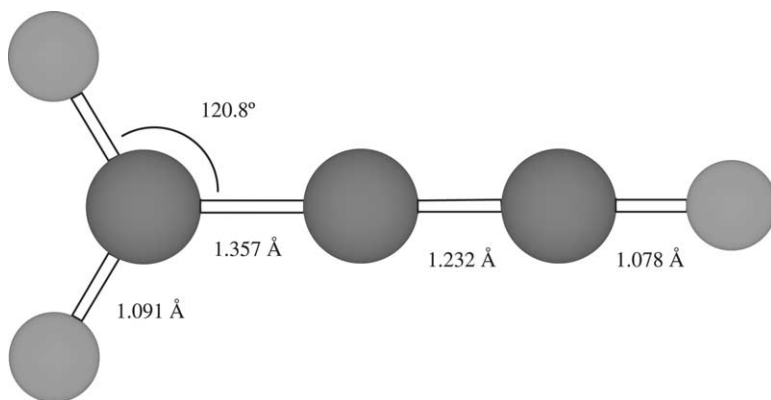


Fig. 24 Structure of 2-propargylium ion, **36**, optimized at the MP2(full)/6-31G(d) level.

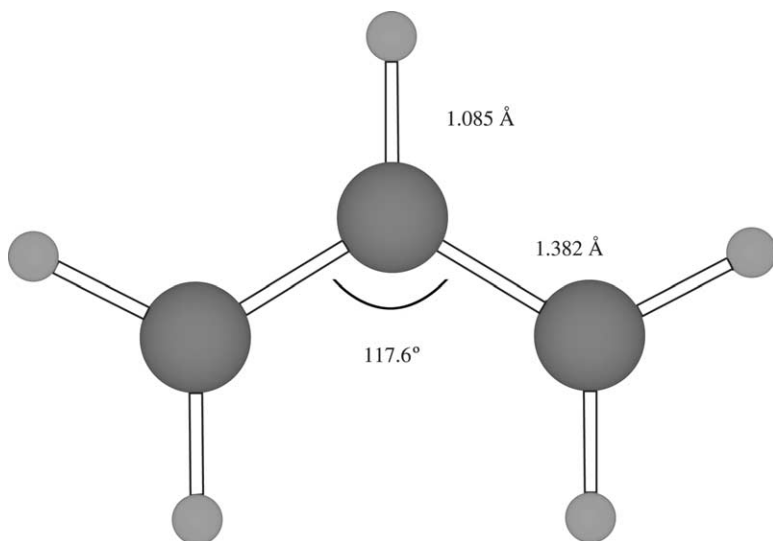


Fig. 25 Structure of 2-propenyl cation, **37**, optimized at the MP2(full)/6-31G(d) level.

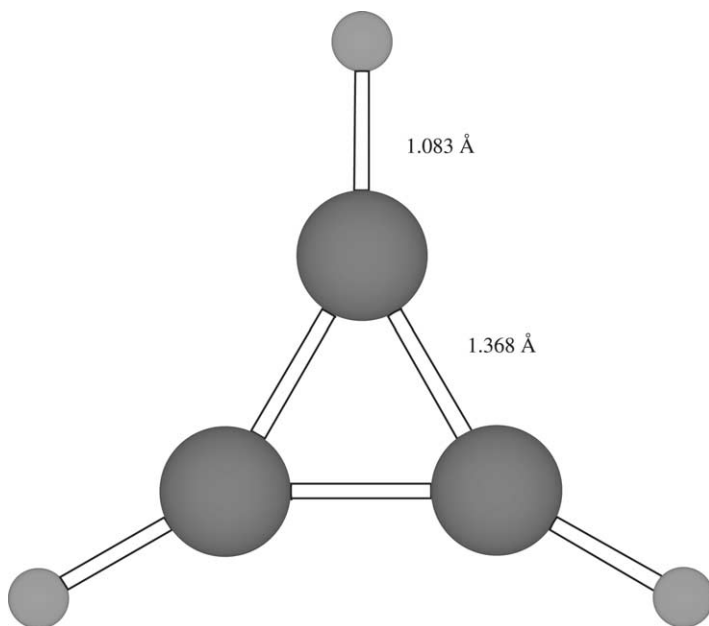


Fig. 26 Structure of cyclopropenyl cation, **38**, optimized at the MP2(full)/6-31G(d) level.

experimental study of the IR and Raman spectra of some of its salts (in liquid sulfur dioxide solution and in polycrystalline state).²¹⁵

$\Delta_f H_m^\circ(\mathbf{38})$ has been obtained experimentally through the determination of the appearance potential of this ion from a variety of neutral precursors including several molecules.²¹³ These studies lead to the values reported in Table 8.

No experimental value of $S_m^\circ(\mathbf{38})$ seems to be presently available. That given in Table 8 was calculated in this work.

Compound **38** has been the subject of a large number of theoretical studies, the most recent ones being listed in Refs. 216–218. The relevant C–C and C–H distances, as obtained at the MP4/6-311G 4* + level,²¹⁶ are, respectively,

Table 8 Thermodynamic data for aromatic and homoaromatic two- and six- π -electron carbenium ions

Cations	$\Delta_f H_m^\circ(\text{g})^a$	$S_m^\circ(\text{g})^b$
Cyclopropenylium (C_3H_3^+) (38)	257.0 \pm 2.0 ^c 256.7 \pm 2.0 ^e 257.2 \pm 2.0 ^f	54.8 \pm 2.0 ^d
Propylcyclopropenylium (<i>c</i> - C_3H_2 - C_3H_7^+) (39)	222.5 \pm 2.9 ^g	85.43 \pm 2.0 ^h
Cyclobutenylium (C_4H_5^+) (<i>c</i> - C_4H_5^+) (42)	210.1 \pm 2.9 ⁱ	59.6 \pm 2.0 ^j
Norbornen-7-ylum (C_7H_9^+) (43)	215.7 \pm 3.3 ^k 215.2 \pm 2.6 ^m	74.2 \pm 2.0 ^l
Norbornadien-7-ylum (C_7H_7^+) (44)	247.9 \pm 3.8 ⁿ 249.9 \pm 2.0 ^p	71.4 \pm 2.0 ^o
Cycloheptatrienylium, tropylium (C_7H_7^+) (45)	211.4 \pm 3.8 ^q 209.8 \pm 2.0 ^s	69.8 \pm 2.0 ^r

^aIn kcal mol^{−1}.

^bIn cal mol^{−1} K^{−1}.

^cFrom appearance energies.²¹³

^dFrom the scaled, symmetry-corrected HF/6-31G* value taken from the G2 calculation (this work).

^eFrom G2 computations.⁹⁹

^fFrom CBS-Q calculations.⁹⁹

^gComputed at the G2(MP2) level (this work); see text.

^hSymmetry-corrected HF/6-31G(d) value taken from the G2(MP2) calculation (this work).

ⁱComputed at the G2 level (this work); see text.

^jSymmetry-corrected HF/6-31G(d) value taken from the G2(MP2) calculation (this work).

^kObtained from the DPA study of the corresponding alcohol and chloride.¹⁸²

^lScaled HF/6-31G(d) value taken from the G2(MP2) calculation (this work).

^mComputed at the G2(MP2) level (this work).

ⁿObtained from the DPA study of the corresponding alcohol.¹⁸²

^oScaled HF/6-31G(d) value taken from the G2(MP2) calculation (this work).

^pComputed at the G2(MP2) level (this work).

^qFrom DPA studies.¹⁵⁶

^rScaled, symmetry-corrected HF/6-31G(d) value (this work).

^sComputational value from Ref. 242.

1.363₂ and 1.079₅ Å. While the latter is close to that in benzene, the former is significantly shorter (C–C bond length of 1.397 Å for benzene). The various vibrational frequencies, including anharmonicity effects and Fermi resonance pairs for this ion and all its deuterated isotopomers, have been computed at extremely high levels and are in excellent agreement with experiment whenever a comparison has been possible.^{216,217}

The fact that the C–C bond lengths are shorter and the C–C stretching frequencies and the delocalization energies per π electron are higher for cyclopropenium than for benzene, is taken as an indication of “superaromaticity”.^{122,215}

The $\Delta_f H_m^\circ(38)$ values computed using G2 methodology¹²² and Petersson’s complete basis technique (CBS-Q)⁹⁹ are nicely consistent and in excellent agreement with experiment (see Table 8).

1-Propylcyclopropen-2-ylum ion (*c*-C₃H₂C₃H₇⁺) (**39**)

To our knowledge, no experimental structural data seem to be available for this ion. The value of $\Delta_f H_m^\circ(39)$ reported in Table 8 was obtained computationally at the G2(MP2) level. The fully optimized structure (of *C_s* symmetry) portrayed in Fig. 27 derives from these calculations.

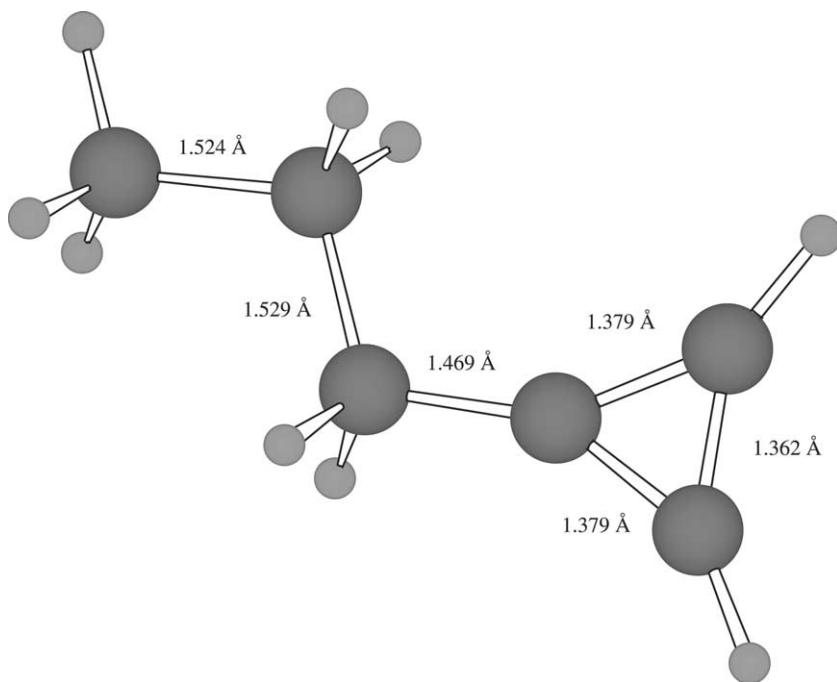


Fig. 27 Structure of 1-propylcyclopropenyl cation, **39**, optimized at the MP2(full)/6-31G(d) level.

1,2-Dipropylcyclopropen-3-ylum [$c\text{-C}_3\text{H}(\text{C}_3\text{H}_7)_2^+$] (**40**) and *tripropylcyclopropenylum* [$c\text{-C}_3(\text{C}_3\text{H}_7)_3^+$] (**41**) ions

Again, no structural data seem to be available for these species. Their optimized structures [MP2(full)/6-31G(d) level; this work], of C_s symmetry, are given in Figs. 28 and 29.

Compounds **40** and **41** were generated by DPA of the corresponding precursors,¹⁵⁶ namely the methyl ethers of 1,2-dipropylcyclopropen-3-ol and tripropylcyclopropen-1-ol. These onsets were anchored to that of the methyl ether of 1,1,1-tricyclopentylcarbinol. An independent onset for 1,1,1-tricyclopentylcarbinol is available so that the onsets of **40** and **41** can be ultimately referred to that of the 1-adamantyl cation. These results, upon the appropriate leaving group correction, provide the values of $\Delta_r G^\circ(25)$ given in Table 4.

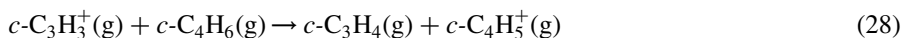
Cyclobutenylum ion ($c\text{-C}_4\text{H}_5^+$) (**42**)

In classical studies, Olah and co-workers²¹⁹ obtained this cation in solution and were able to show that at -110°C it has a puckered structure (Fig. 30) displaying true aromatic delocalization. Compound **42** is thus the simplest homoaromatic system.^{220–222}

This aromatic character was confirmed by an extensive series of high-level quantum mechanical studies (structure, energetics and NMR chemical shifts) by Schleyer and co-workers.²²³

G2 studies have been recently performed on **42** and cyclobutadiene.²²⁴

To our knowledge, there is no experimental information on the thermodynamics of this ion. The results we present in Table 8 are based on our own G2 calculations for reaction (28), the hydride exchange between cyclopropenylum and cyclobutenylum ions:



Norbornen-7-ylum ion (C_7H_9^+) (**43**)

The discovery by Winstein, Woodward, and coworkers of a 10^{11} rate enhancement in the solvolysis of *anti*-7-norbornenyl tosylate relative to that of 7-norbornyl tosylate²²⁵ led to extensive investigations of this ion.

The ^1H ^{226,227} and ^{13}C NMR spectra of **43**²²⁸ and some of its derivatives²²⁹ in solution at low temperature are known. These spectra as well as the X-ray structure of 7-phenyl-2,3-dimethyl-7-norbornenyl cation²³⁰ indicate that C(7) in **43** is “canted” towards the formal double bond, implying a significant degree of homoconjugation (Fig. 31).

Ab initio studies^{231,232} fully agree with these contentions and further, through computation of the ^{13}C NMR shifts, lead to an entirely consistent image of this ion as a species of C_s symmetry.

Thermodynamic data for this species (see Table 8) were obtained from the DPA study of *anti*-7-norbornenyl chloride and *anti*-7-norbornenol¹⁸² with the appropriate

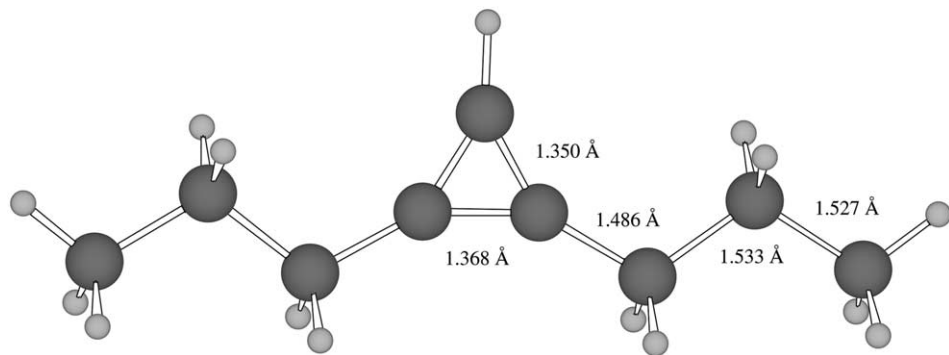


Fig. 28 Structure of 1,2-Dipropylcyclopropen-3-ylum ion, **40**, optimized at the MP2(full)/6-31G(d) level.

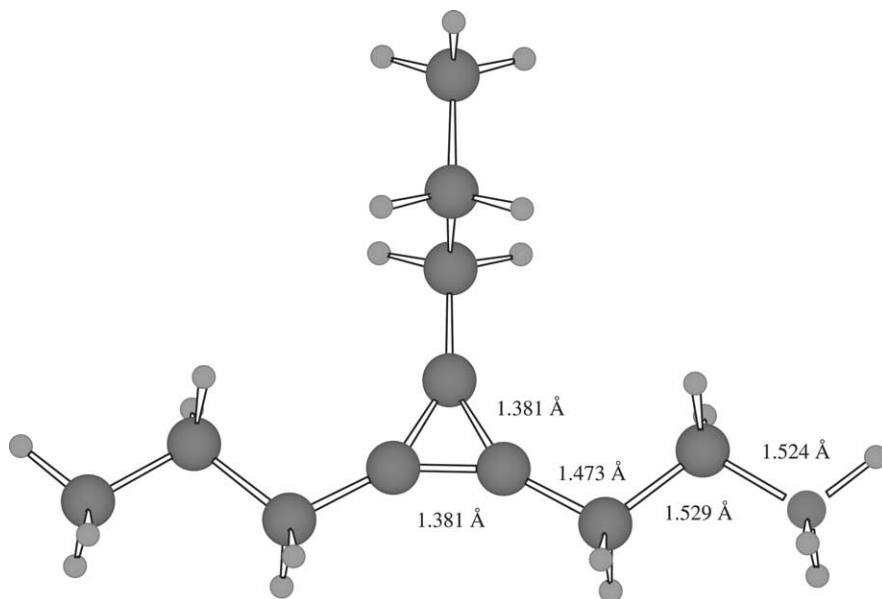


Fig. 29 Structure of tripropylcyclopropenyl, **41**, optimized at the MP2(full)/6-31G(d) level.

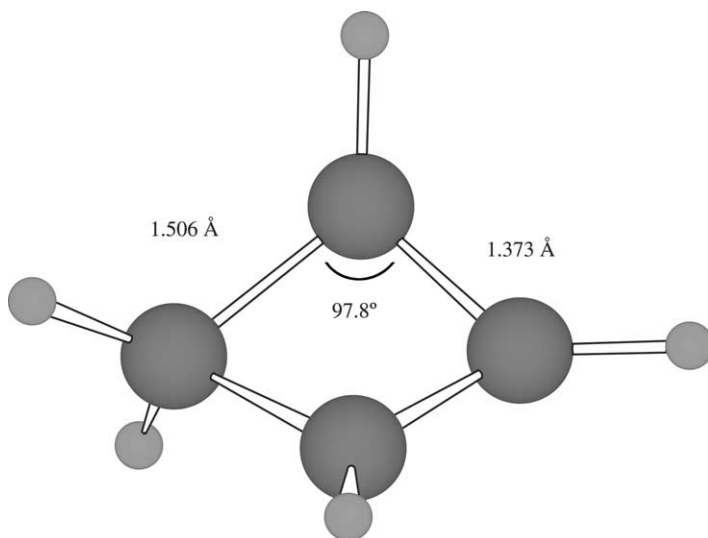


Fig. 30 Structure of cyclobutenyl cation, **42**, optimized at the MP2(full)/6-31G(d) level.

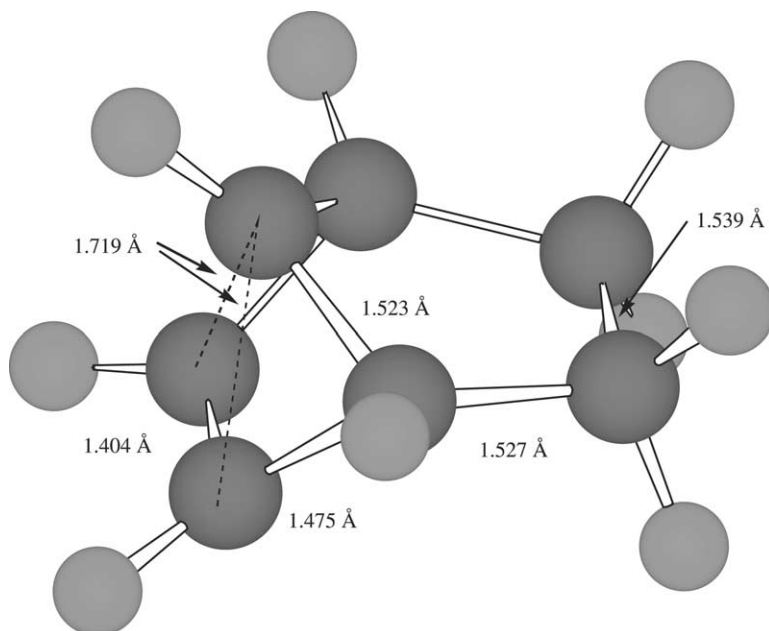


Fig. 31 Structure of norbornen-7-ylum ion, **43**, optimized at the MP2(full)/6-31G(d) level.

corrections. We present in Table 8 thermodynamic data for **43** obtained at the G2(MP2) level in this work. The results are extremely consistent. $\Delta_r G_m^\circ(25)$ is given in Table 4.

Norbornadien-7-ylum ion ($C_7H_7^+$) (**44**)

7-Norbornadienyl chloride solvolyzes some 10^3 times faster than *anti*-7-norbornenyl chloride.²³³ This enormous neighboring group participation is associated with the intrinsic stability of **44**. This ion has also been studied by NMR in solution at low temperature.^{226,227} These experiments as well as *ab initio* studies^{231,232} indicate that the most stable structure of **44** corresponds to that presented in Fig. 32. This is a structure of C_s symmetry, the more symmetrical C_{2v} structure being the transition state between the two C_s mirror images.²³⁴

Experimental thermodynamic data for **44** (see Table 8) were obtained from the DPA study of 7-norbornadienol.¹⁸² $\Delta_r G_m^\circ(25)$ is given in Table 4. Thermodynamic data for **44** obtained at the G2(MP2) level in this work are given in Table 8.

SIX-ELECTRON AROMATIC IONS

Cycloheptatrienylum ion (tropylium) ($C_7H_7^+$) (**45**)

The synthesis and description of some important properties (including its very simple IR spectrum, a consequence of the D_{7h} symmetry) of this ion were carried out

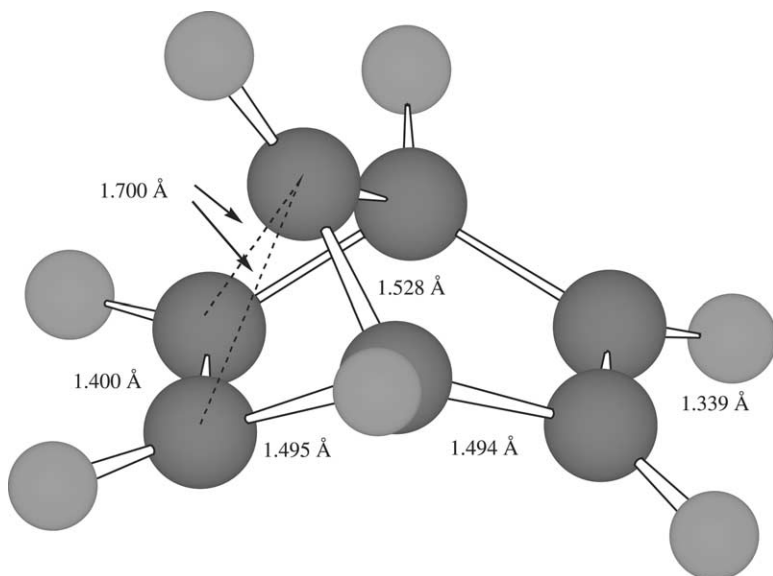


Fig. 32 Structure of norbornadien-7-ylum ion, **44**, optimized at the MP2(full)/6-31G(d) level.

in 1954 by Doering and Knox²³⁵ even though it was actually prepared unintentionally, but not identified, in 1881.²³⁶ Interest in this and other species originates in Hückel's classical studies²³⁷ ($4n + 2\pi$ -electron rule).

The remarkably simple ^1H and ^{13}C NMR spectra of **45** in solution are known^{238, 239} as is its X-ray structure (in salts).^{240,241}

The thermodynamic data for this ion as reported in Table 8 were obtained from the following sources:

- (1) The DPA study of tropylium methyl ether, $\text{C}_7\text{H}_7\text{OCH}_3$, with the appropriate leaving group corrections.¹⁵⁶
- (2) The G2(MP2) results from Nicolaides and Radom.²⁴²

The experimental determination of $\Delta_f H^\circ_m(\mathbf{45})$ has long been marred, *inter alia*, by the interconversion of the molecular ions of toluene and cycloheptatriene prior to dissociation.^{243,244} The experimental adiabatic ionization energy of the tropylium radical,^{245,246} has been found to be in excellent agreement with the result of high-level *ab initio* calculations,^{247,248} but the computed standard enthalpy of formation of the radical seems significantly different from the reported experimental value.^{247,248} It is thus rewarding to find that both DPA and computed values are in excellent agreement. The structure portrayed in Fig. 33 was optimized at the MP2(full)/6-31G(d) level in this work. The value of $\Delta_f G^\circ(25)$ reported in Table 4 is from our DPA studies corrected with the corresponding leaving group corrections.

PHENYL-SUBSTITUTED CARBOCATIONS

Benzylum ion ($C_7H_7^+$) (**46**)

To our knowledge, **46** has never been observed in solution under stable conditions, even at low temperature. Pulse radiolysis²⁴⁹ of benzyl chloride as well as flash photolysis²⁵⁰ of several derivatives in HFIP have allowed the observation of the electronic absorption spectra of benzyl and its 4-methyl and 4-methoxy derivatives. The 1H and ^{13}C NMR spectra of the 2,4,6-trimethylbenzyl cation and other more heavily substituted benzyl cations, however, have been studied at low temperature in superacid media.²⁵¹ In the gas phase, cold benzyl radical has been probed by two-color, resonant two-photon ionization techniques, thus providing very accurate vibrational frequencies below 650 cm^{-1} for the benzyl cation.²⁵² Furthermore, the adiabatic ionization energy of benzyl radical and several isotopomers in the ground state were determined from their threshold photoionization spectra using resonant two-photon excitation and detection of electrons by pulsed field ionization.²⁵³ This information, combined with $\Delta_f H_m^\circ(C_6H_5CH_2)$ from Ref. 212 leads to the value of $\Delta_f H_m^\circ(\mathbf{46})$ reported in Table 9.

Data for this ion were also obtained through the study of hydride and chloride exchange with ions of known stability using both HPMS²⁵⁴ and FT ICR.^{51,52} These results, also reported in Tables 9 and 4, respectively, are rewardingly coincident. This is particularly important because it tends to indicate that the well-known benzyl/tropylium isomerization problem²⁴⁴ does not seem to affect significantly these results

The study of substituent effects on the stability of substituted benzyl cations^{51,52,149} is important as a source of thermodynamic information as well as a means to provide a conceptual link between the stabilities of a number of important carbocations. Mishima's study,⁵¹ in particular, shows that the stabilities in terms of standard Gibbs energy for 4-methoxy- and 4-nitro-substituted benzyl cations differ by some $24.9\text{ kcal mol}^{-1}$. The former has a stability comparable to that of bicyclo[3.3.3]undecyl (manxyl) cation, while the latter is comparable to the *c*-pentyl cation. We present these two extreme cases in Table 4. The relative stabilities of other substituted benzyl cations are given in Refs. 50 and 51.

The results of high-level *ab initio* calculations on this C_{2v} ion (Fig. 34) are also summarized in Table 9. G2-level computations lead to $\Delta_f H_m^\circ(g)$ values in excellent agreement with experiment.²⁴² Equally satisfactory are the results obtained at the G2(MP2,SVP) level for the ionization potential of benzyl radical.²⁴⁸

1-Phenylethan-1-ylum ion, α -phenethyl cation ($C_8H_9^+$) (**47**)

As far as we are aware, **47** has not been observed as a stable species in solution, although flash photolysis²⁵⁰ of ethylbenzene and several of its derivatives in HFIP has allowed the detection of their electronic absorption spectra in the near-UV-visible region.

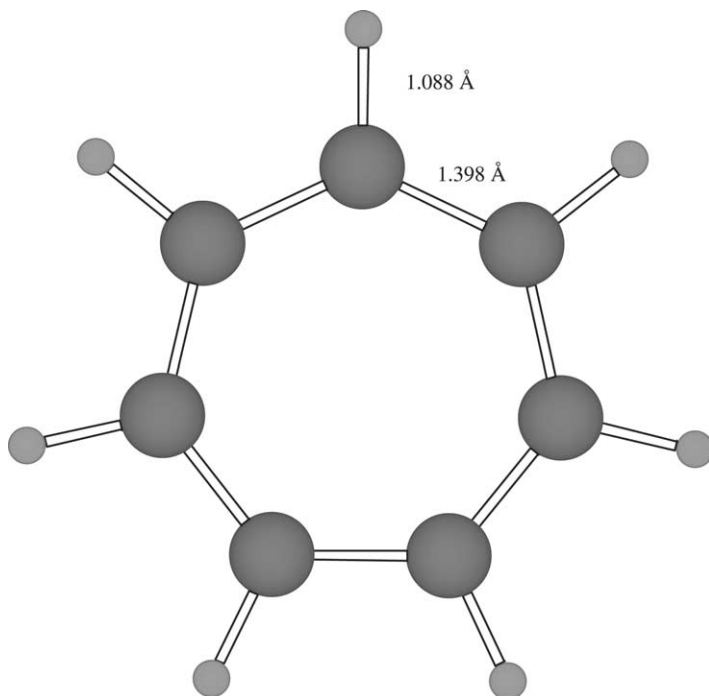


Fig. 33 Structure of cycloheptatrienylium (tropylium) ion, **45**, optimized at the MP2(full)/6-31G(d) level.

$\Delta_f H_m^\circ(\mathbf{47})$ can be obtained from the experimental PA and GB of styrene. Over the years, a number of values has been obtained, essentially by HMPS and ICR. Here, we use the average value recommended in Ref. 43. Values are also available from the FT ICR study⁵¹ of chloride exchange between this ion and the *tert*-butyl cation (through the appropriate ladder of experimental values). As shown in Table 9, the results are extremely self-consistent.

We present in Fig. 35 the structure (C_s symmetry) optimized at the MP2(full)/6-31G(d) level (this work). Recently, a large computational study has been published on benzyl and larger carbocations.¹⁵⁵ It uses both the optimized force field MMP2 extended to carbocations and MP4sdq/6-31G(d)//MP2(full)/6-31G(d) calculations. It provides, *inter alia*, valuable estimates of standard heats of formation. In this case, the difference in stability between phenethyl and 4-methylbenzyl cations (1.7 by *ab initio* computations and 2.9 kcal mol⁻¹ by MMP2) is in good agreement with the experimental results in Ref. 51. Our own G2(MP2) results are presented in Table 9.

The experimental $\Delta_f G^\circ(25)$ for this ion is given in Table 4.

Table 9 Thermodynamic data for phenyl-substituted carbocations

Cations	$\Delta_f H_m^\circ(\text{g})^a$	$S_m^\circ(\text{g})^b$
Benzylum (C_7H_7^+) (46)	216.8 \pm 0.6 ^c 216.8 \pm 2.0 ^e	74.6 \pm 2.0 ^d
1-Phenylethan-1-ylum (C_8H_9^+) (47)	200.2 \pm 2.0 ^f 200.6 \pm 2.0 ^g 198.7 \pm 2.0 ⁱ	84.7 \pm 2.0 ^h
2-Phenylpropan-2-ylum ($\text{C}_9\text{H}_{11}^+$) (48)	187.4 \pm 2.0 ^j 187.2 \pm 2.0 ^k	93.1 \pm 2.0 ^l
Diphenylmethanylium ($\text{C}_{13}\text{H}_{11}^+$) (49)	225.7 \pm 2.0 ^m	99.7 \pm 2.0 ⁿ
1,1-Diphenylethan-1-ylum ($\text{C}_{14}\text{H}_{13}^+$) (50)	212.7 \pm 2.3 ^o 214.1 \pm 2.0 ^q	107.9. \pm .2.0 ^p
Triphenylmethanylium ($\text{C}_{19}\text{H}_{15}^+$) (51)	243.7 \pm 2.0 ^r	123.8 \pm 2.0 ^s

^aIn kcal mol⁻¹.^bIn cal mol⁻¹ K⁻¹.^cFrom Ref. 212. See text.^dScaled, symmetry-corrected HF/6-31G(d) value (this work).^eComputed (G2) value from Ref. 242.^fFrom the averaged experimental GB(styrene), 193.4 kcal mol⁻¹ (Ref. 43), and the entropy correction from the same reference.^gFrom the standard Gibbs energy change for the formal hydride exchange between α -phenethyl and *tert*-butyl cations as determined by FT ICR in Ref. 51. Entropies corrected using the experimental values for *iso*-butene²⁶ and styrene²⁶ (82.48 cal mol⁻¹ K⁻¹) and our computed value for the phenethyl cation.^hScaled HF/6-31G(d) value from this work.ⁱCombining experimental values for $\Delta_f H_m^\circ$, $\text{C}_6\text{H}_5\text{--CH}_2\text{CH}_3$, *iso*-butane and **6** with the standard enthalpy for the hydride exchange between **6** and **47**.^jFrom the averaged experimental PA(α -methyl styrene), 206.6 kcal mol⁻¹ (Ref. 43) and $\Delta_f H_m^\circ$ (C_9H_{10}) = 28.27 \pm 0.34 kcal mol⁻¹.²⁶^kComputed (MMP2) value from Ref. 155.^lScaled, symmetry-corrected value at the HF/6-31G(d) level (this work).^mMMP2 value from Ref. 155.ⁿScaled, symmetry-corrected value at the HF/6-31G(d) level (this work).^oFrom the averaged experimental PA (1,1-diphenylethylene), 211.7 kcal mol⁻¹ (Ref. 43) and $\Delta_f H_m^\circ$ ($\text{C}_{14}\text{H}_{12}$) = 58.7 \pm 1.1 kcal mol⁻¹.²⁶^pScaled, symmetry-corrected value at the HF/6-31G(d) level (this work).^qMMP2 value from Ref. 155.^rMMP2 value from Ref. 155.^sScaled, symmetry-corrected value at the HF/6-31G(d) level (this work).

2-Phenylpropan-2-ylum ion, cumyl cation ($\text{C}_9\text{H}_{11}^+$) (**48**)

This ion as well as its derivatives have played a key role in the development of current concepts and quantitative treatment of substituent effects on organic reactivity.^{256,257}

The UV–visible absorption spectra of **48** and some 4-substituted derivatives have been obtained in HFIP solution using laser flash photolysis techniques.²⁵⁸ The ¹H

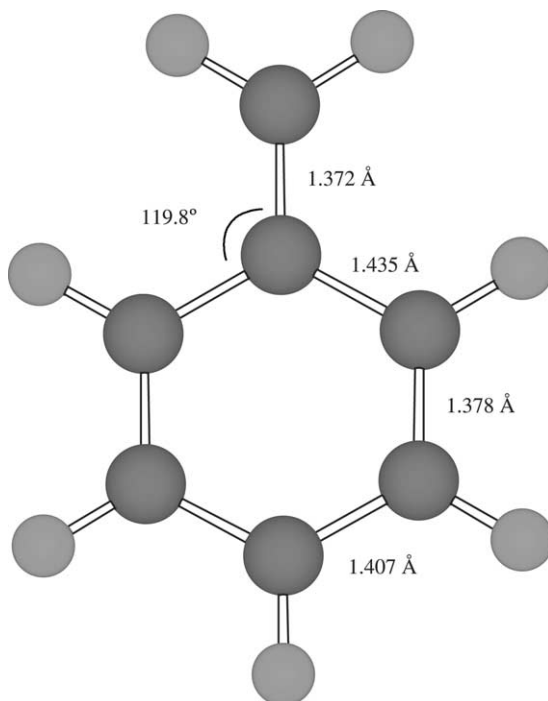


Fig. 34 Structure of benzylum ion, **46**, optimized at the MP2(full)/6-31G(d) level.

NMR spectrum of this ion at low temperature and in superacid media was obtained in 1964^{259,260} and carefully analyzed in 1966.²⁶¹ The X-ray structure of its hexafluoroantimonate(V) salt was obtained much more recently²⁶² and it reveals significant benzylic delocalization.

The $\Delta_f H_m^\circ(\text{g})$ value reported in Table 9 was obtained from the PA recommended in Ref. 43, based on ICR data from Taft's and Marshall's groups.

We present in Fig. 36 the C_{2v} structure of **48**, obtained at the MP2(full)/6-31G(d) level (this work).

The experimental $\Delta_f H_m^\circ(\text{48})$ is in quite good agreement with the computed MMP2 and MP4sdq/6-31G(d)//MP2(full)/6-31G* results from Ref. 155 (see Table 9).

We report in Table 4 the experimental $\Delta_r G^\circ(25)$ for this ion as given in Refs. 51 and 52. Also reported are values for 4-methoxy and 3-nitro cumyl cations, taken from the same references. These are extreme cases of substituent effects in these systems and span a range of stabilities somewhat smaller than that of the homologous benzyl derivatives (19.9 versus 24.3 kcal mol⁻¹). Still, this yields a stability for the 4-methoxy derivative quite close to that of trityl cation.

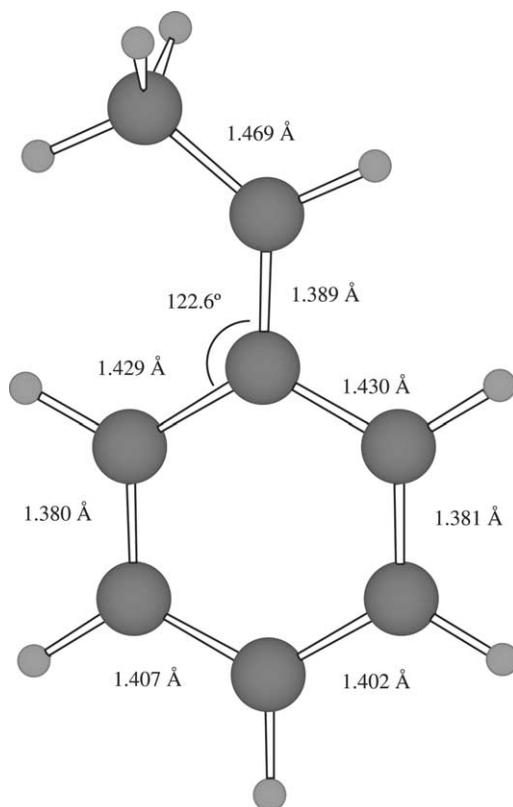


Fig. 35 Structure of 1-phenylethan-1-ylum ion, **47**, optimized at the MP2(full)/6-31G(d) level.

*Diphenylmethanylium ion, benzhydryl cation (C₁₃H₁₁⁺) (**49**)*

The ¹H NMR spectrum of this ion was reported in the early 1960s^{259,260} and analyzed a little later.²⁶¹

This ion and several ring-substituted derivatives have been generated by nanosecond laser flash photolysis in solution.²⁶³

As far as we know, **49** has not yet been studied in the solid state.

Direct experimental determinations of its thermodynamic state functions are still missing. Fortunately, a fairly reliable value for $\Delta_f H_m^\circ(\mathbf{49})$ is available thanks to the MMP2 and MP4sdq/6-31G(d)//Mp2(full)/6-31G(d) calculations in Ref. 155. This value is presented in Table 9. The value of $\Delta_r G^\circ(25)$ given in Table 4 as well as the structure in Fig. 37 were obtained in this study.

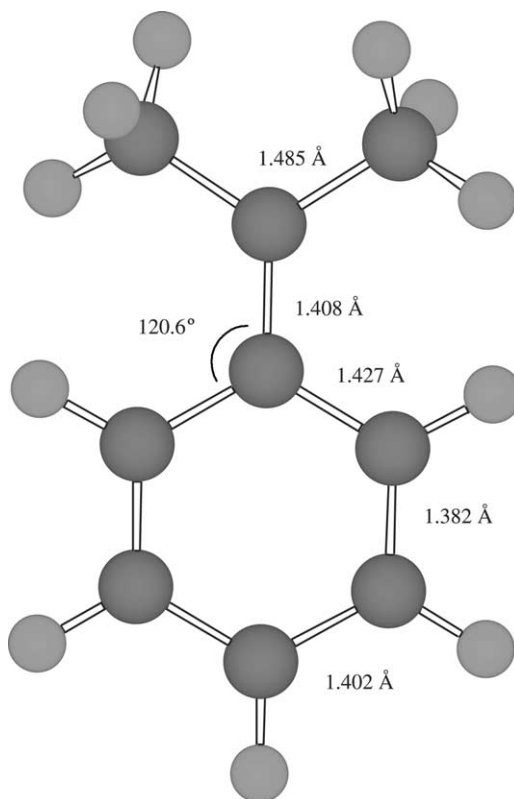


Fig. 36 Structure of 2-phenylpropan-2-ylum ion, **48**, optimized at the MP2(full)/6-31G(d) level.

1,1-Diphenylethan-1-ylum ion ($C_{14}H_{13}^+$) (**50**)

This ion is known in solution at low temperature in strongly acidic media and was generally studied together with benzhydryl cation.^{259–261}

Its UV–visible spectrum has been obtained by laser flash photolysis techniques.²⁵⁸ Interestingly, it has recently been generated and studied encapsulated in zeolites²⁶⁴ and at ambient temperature in superacid molten salts.²⁶⁵

The experimental $\Delta_f H_m^\circ$ (**50**) given in Table 9 was obtained from the GB of 1,1-diphenylethane as determined by Taft's group and reported in Ref. 43. This value is in agreement with the computational result from Ref. 155.

We present in Table 4 the $\Delta_r G^\circ(25)$ obtained in this study and based on the experimental data indicated above. The structure optimized at the MP2(full)/6-31G(d) level portrayed in Fig. 38 was also obtained in this work.

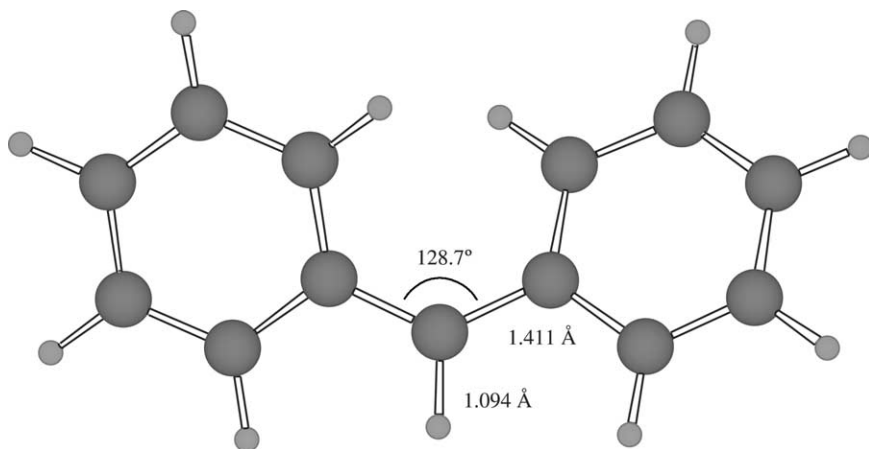


Fig. 37 Structure of diphenylmethanylium ion, **49**, optimized at the MP2(full)/6-31G(d) level.

*Triphenylmethanylium ion, triphenyl methyl cation (C₁₉H₁₅⁺) (**51**)*

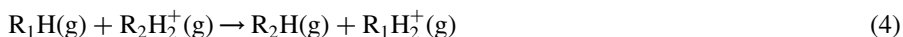
This species^{266–268} as well as the salt character of some of its derivatives have long been known.^{269,270} Structure **51** has been studied by UV–visible²⁷¹ and IR²⁷² spectroscopies. Its ¹H NMR spectrum in solution was reported in 1959²⁷³ and its features carefully discussed in 1966.²⁶¹ The ¹³C NMR spectrum in superacid solution was also reported in 1964.²⁷⁴ It has also been obtained in the solid state, trapped in a zeolite.²⁷⁵ The ¹³C NMR spectra of a number of other triaryl and heteroaryl ions have also been reported.²⁷⁶

All these techniques as well as the X-ray spectra of its salts²⁷⁷ agree on the twisting of the phenyl rings out of the central carbon plane by *ca.* 33°. Figure 39 presents the structure of this ion (symmetry group *D*₃) obtained at the MP2(full)/6-31G(d) level in this work. Our calculated structure agrees nicely with this result and with the MMP2 structure.¹⁵⁵

The $\Delta_f H^\circ_m(\mathbf{51})$ given in Table 9 was obtained computationally at the MMP2 level¹⁵⁵ and was used to estimate the value of $\Delta_f G^\circ(25)$ given in Table 4.

6 Solution reactivity

Consider reactions (3a) and (4):



For comparison purposes it seems useful to take the cumyl cation **48** as a reference ion, on account of the fact that it can be obtained through reactions (29) and (30) and

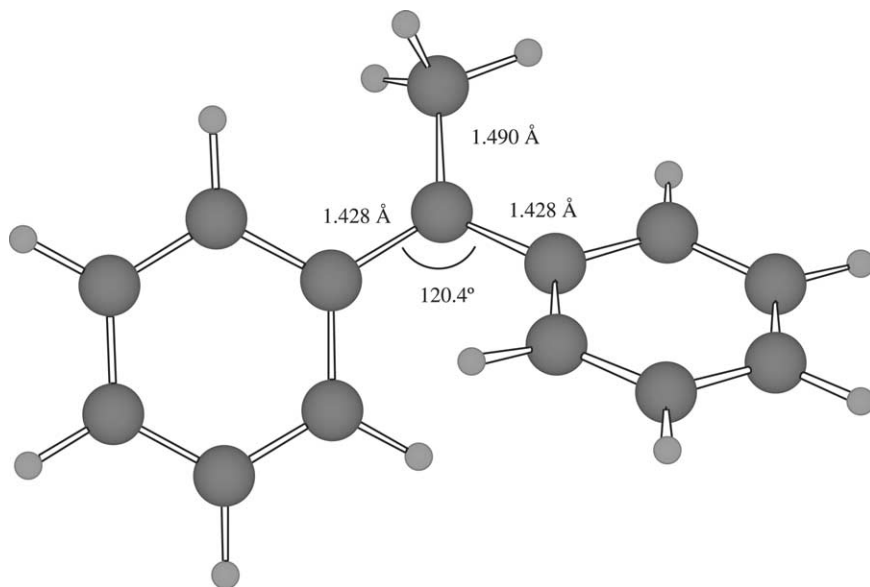
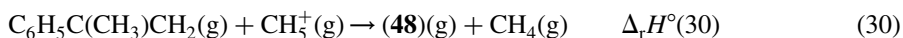
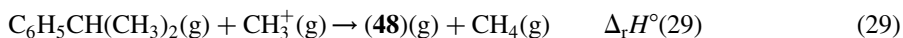


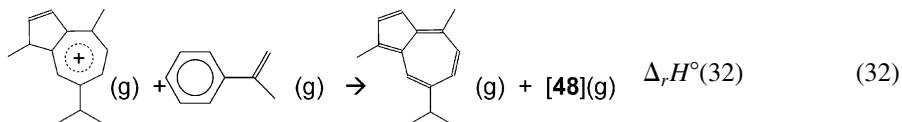
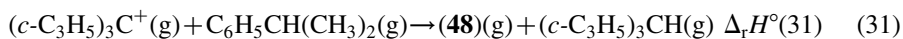
Fig. 38 Structure of 1,1-diphenylethan-1-ylum ion, **50**, optimized at the MP2(full)/6-31G(d) level.

that in both cases, fairly reliable thermodynamic data are available for reactants and products:



Using data given in the previous sections, we get $\Delta_r H^\circ(29) = -93.3 \pm 2.1$ and $\Delta_r H^\circ(30) = -76.8 \pm 2.2 \text{ kcal mol}^{-1}$.

Let us now examine two rather extreme cases: the hydride exchange between tricyclopropylmethyl and cumyl cations and the proton exchange between guaiazulene²⁷⁸ and α -methylstyrene, respectively (reactions 31 and 32):



The corresponding $\Delta_r H^\circ(31)$ and $\Delta_r H^\circ(32)$ are, respectively, -11.0 ± 4.1 and $28.4 \pm 2.8 \text{ kcal mol}^{-1}$.²⁷⁹

These results show that the range of structural effects on the intrinsic (gas phase) stability of carbenium ions amounts to at least $110 \text{ kcal mol}^{-1}$. Let us see now how

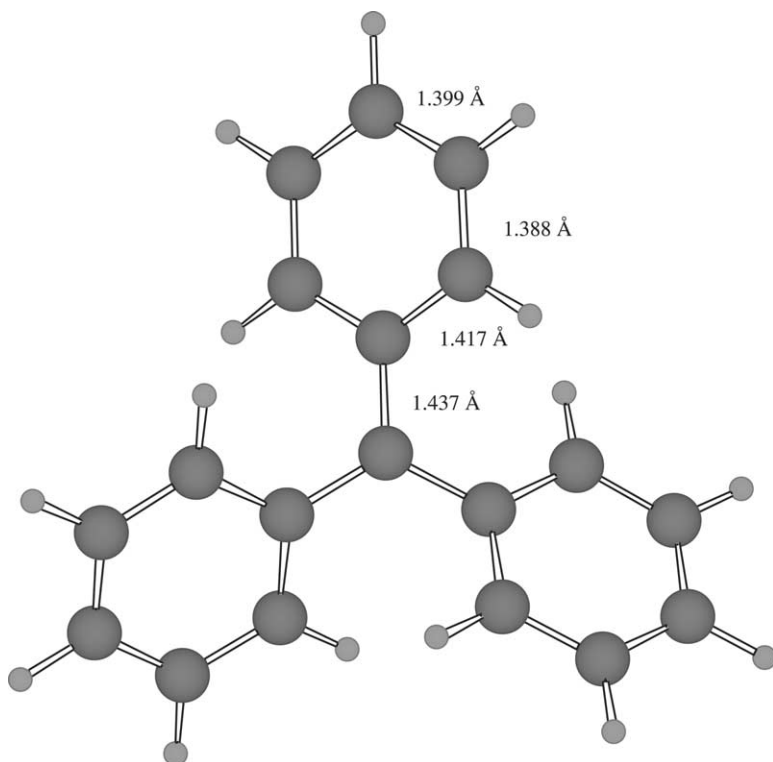


Fig. 39 Structure of triphenylmethanylium ion, **51**, optimized at the MP2(full)/6-31G(d) level.

the differences in intrinsic stability affect solution (“real world”?) reactivity. As in the previous section, thermodynamic criteria seem well suited for this purpose and so are kinetic data, through formally straightforward extra thermodynamic relationships.

THERMODYNAMIC PROPERTIES

The pK_{R^+} and pK_a scales

The use of reaction (33) in solution as a quantitative tool for the ranking of carbocation stability is at least half-a-century old:²⁸⁰



The concept is extremely simple, as it takes as its starting point the equilibrium constant for this reaction, K_{R^+} ^{157,281,282}

$$K_{R^+} = a_{R^+} a_{H_2O} / a_{ROH} a_{H^+} \quad (34)$$

Given two alcohols, respectively, R_1OH and R_2OH , the position of equilibrium (35)



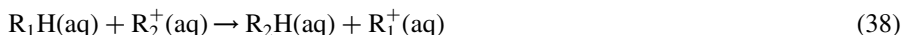
is simply given by K_{35} , equation (36):

$$K_{35} = K_{R(1)^+} / K_{R(2)^+} \quad (36)$$

or

$$\log K_{35} = pK_{R(1)^+} - pK_{R(2)^+} \quad (37)$$

Reaction (38) is also suitable for comparison purposes. Following the same procedure as above, $\log K_{38}$ is given by equation (39):



$$\log K_{38} = pK_a(R_1) - pK_a(R_2) \quad (39)$$

From an operational point of view, difficulties might arise from the fact that rather high acid concentrations and/or aqueous-organic solvents are often used in these studies, the reference state being the pure water solution. These shortcomings can be averted by the use of appropriate methods, recently reviewed by Cox in this series.²⁸³

In what follows we shall use both the pK_{R^+} and pK_a scales for the quantitative comparison of carbenium ions, without attempting any correction for aqueous-organic medium effects. All data are anchored to **48**. Taft and co-workers already compared gas phase and solution basicities of ethylenic and aromatic hydrocarbons.^{278,284} Now the pK_{R^+} scale has been widely extended^{285,286} through the determination of K_{R^+} from the reaction rate constants for the forward and reverse processes in reaction (33). This is a very important breakthrough. Also, a number of new data for other species in the gas phase has become available.

We can now carry out a comparison of solution and gas-phase rankings of stabilities, respectively, using ΔpK_{R^+} and ΔpK_a values; i.e., referred to processes leading to **48**. The reference processes in the gas phase are the chloride exchange between **48** and the relevant ion, i.e. reaction (40), and the proton exchange between α -methylstyrene and the relevant base, i.e. reaction (41). $\Delta_r G^\circ$ values for both reactions are given, respectively, by the differences in $\Delta_r G^\circ(25)$ for the corresponding chloride and cumyl chloride (data from Table 4) and the difference in GB values between the relevant base and α -methylstyrene. Formally, very similar processes are compared as they only differ in the leaving group:

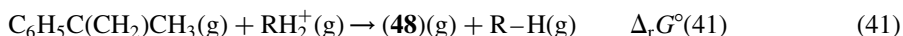
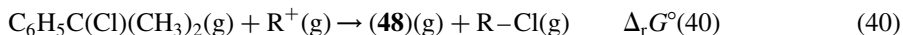


Figure 40 is a joint plot of ΔpK_{R^+} and ΔpK_a (using data from Refs. 278, 284–287) against $\Delta_r G^\circ(40)$ and $\Delta_r G^\circ(41)$. Squares denote $\Delta pK_a / \Delta_r G^\circ(41)$ and open circles denote $\Delta pK_{R^+} / \Delta_r G^\circ(40)$. They define a straight line of very good statistical quality involving ranges of some 45 kcal mol⁻¹ and 27 log units, respectively. The level of

self-consistency of these results is both rewarding and surprising, on account of the variety of experimental methods involved. Conversion of log units to Gibbs energies leads to a slope of 0.77.

We take this result as implying that: (1) the ranking of intrinsic stabilities of these ions is faithfully reproduced in solution with a moderate attenuation (*ca.* 24%); (2) the ionic systems described by this line follow a constant pattern of solvation which we call “general” for the sake of simplicity. This does not mean that these effects are small in absolute value but rather, that *differential* solvation effects are likely to be small; and (3) the fact that the slope is smaller than unity suggests that solvation energetics are not exactly constant and that the less stable ions interact more strongly with the solvent. The correlation spans a range of stabilities going all the way from benzylium to tripropylcyclopropenylum ion. Table 4 shows that this range includes most tertiary alkyl cations, several stabilized secondary ones, a number of bridgehead carbocations and phenyl- and cyclopropyl-stabilized methyl cations. This correlation appears, therefore, as a very powerful and simple unifying factor.

Ions **38**, **49**–**51** do not seem to follow the “general” pattern and were not included in the correlation. Interestingly, at least the gas-phase data for **38**, the cyclopropenylum ion, seem quite reliable. This ion, however, is small and readily accessible to solvent molecules. Furthermore, *ab initio* calculations indicate that **38** is a strong hydrogen bond donor to water. It seems reasonable to attribute at least part of this enhanced stability in solution to hydrogen bonding to the solvent. A plot similar to Fig. 40 but involving standard Gibbs energy changes for hydroxide instead of chloride exchange is also nicely linear and, once again, **38** is deviant but **49**–**51** are now “well behaved”. This is important, inasmuch as the pK_{R+} is based on the protonation of alcohols and strongly suggests that these ions do not display any abnormal behavior in solution. It follows that the departures shown in Fig. 40 originate in the leaving group correction for the corresponding chlorides. At this point, unfortunately, the possibility for these corrections being affected by computational artifacts cannot be ruled out.

Ions with pK_{R+} values of about 14 have recently been synthesized.²⁸⁸ Assuming that the linearity extends up to these ions, this would bring the range of structural effects on stabilities of carbenium ions to at least 120 kcal mol^{−1}.

Solution thermochemistry

The quantitative thermodynamic study of the ionization of appropriate precursors R–X (X = OH, halogen) by superacidic species (FSO₃H, SbF₅, FSO₃H–SbF₅ mixtures) in low nucleophilicity solvents [SO₂(l), SO₂ClF, CH₂Cl₂] at low temperatures was carried out during the 1970s and early 1980s by Arnett and co-workers.²⁸⁹ The basic concept behind this effort was “to provide the basis for a single stability scale in solution ranging from the relatively unstable secondary ions (e.g., isopropyl or cyclopentyl) to the more familiar triarylmethylcarbenium ions. If this were accomplished, future workers could use a scale to interpolate and include

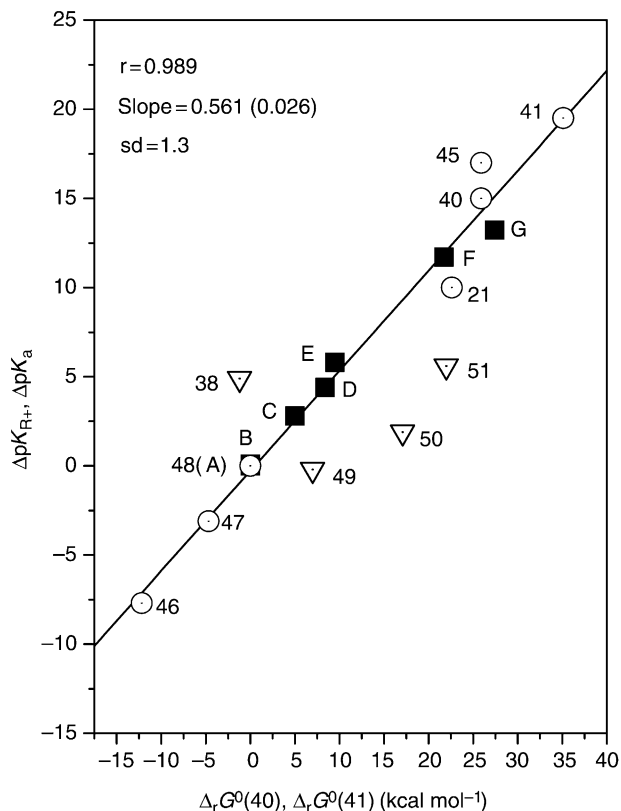


Fig. 40 Plot of ΔpK_{R^+} and ΔpK_a (i.e., values relative to **48** and α -methylstyrene) versus $\Delta_r G^\circ(40)$ and $\Delta_r G^\circ(41)$. Open circles denote $\Delta pK_{R^+}/\Delta_r G^\circ(40)$ and full squares denote $\Delta pK_a/\Delta_r G^\circ(41)$. A = α -methylstyrene; B = hexamethylbenzene; C = 1,1-diphenylethylene; D = 1,1'-ethenyldienebis-[4-methyl-benzene]; E = 1,1-dicyclopropylethylene; F = azulene; G = guaiazulene.

almost any ion whose ionization energy can be related directly or indirectly to the gas phase scale, the pK_R scale, thermochemical scales or solvolysis rates".²⁹⁰

We present in Fig. 41 a plot of the ionization enthalpies of alcohols in a 1:1 mixture of SbF_5 and FSO_3H in SO_2ClF solution,²⁹⁰ ΔH°_i , against $\Delta_r G^\circ(25)$. The proportionality is very clear but the scatter is significant. More limited groups of ions yield better correlations, particularly in the case of the ionization of chlorides by SbF_5 .²⁹¹ Entropic factors might play a role, as well as, in some cases, ion-pairing. Differential solvation effects in these systems are well known. Thus, adamantyl appears as less stable than the *tert*-butyl cation while the opposite occurs in the gas phase. We have recently shown computationally that at least part of this reversal can be largely attributed to solvation effects.⁶⁸ It was shown, much earlier, that the

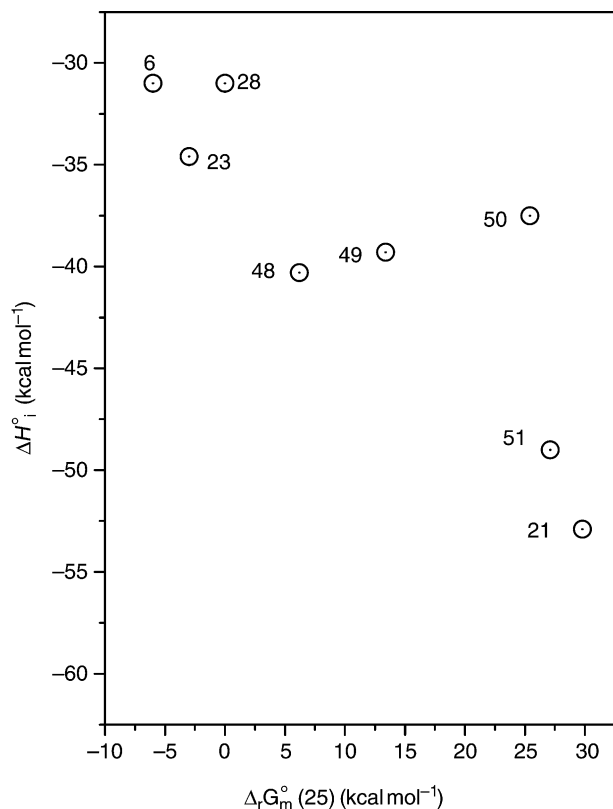


Fig. 41 Enthalpies of ionization, ΔH_i° for alcohols with 1:1 mixtures of SbF_5 and FSO_3H in SO_2ClF solution versus $\Delta_r G^\circ(25)$.

ranking of basicities of alkylbenzenes was reversed on going from the gas phase to superacid solutions,²⁹² a fact also consistent with solvation effects.

As things stand now, a more complete understanding of the situation still requires considerable work.

REACTION KINETICS

It is generally accepted that $\text{S}_\text{N}1$ solvolysis rates for a series of similar compounds under similar conditions reflect directly the stability of their carbocationoid intermediates.^{166,293} However, the lack of reliable experimental data for stabilities of carbenium ions prevented verification of this hypothesis for a long time. Several approaches at various levels of sophistication were advanced to estimate these ion stabilities: their strain was estimated via empirical correlations with IR-stretching frequencies of the respective carbonyl groups, and non-bonded interactions from molecular models or, subsequently, by empirical force-field calculations.^{294–302}

However, owing to the empirical nature of these methods, the significance of the results could not be truly assessed. More recently, Arnett *et al.*^{109,290} reported heats of ionization (ΔH_i) of alkyl chlorides to stable carbocations in SbF_5 –solvent mixtures. Correlation of the heats of ionization with the respective free energies of activation for ethanolysis afforded a straight line over a range of 22 kcal mol^{-1} for ΔH_i .

Initial attempts to establish an analogous correlation between solvolytic reactivity for a limited series of bridgehead halides and stability of the respective carbenium ions in the gas phase by ion cyclotron resonance (ICR) were met by only limited success owing to apparent rearrangement of some of the ions under the conditions of the ICR experiments.³⁰³ Although highly strained ions such as 1-norbornyl were particularly prone to undergo such rearrangements, the ICR measurements alone did not allow a distinction between unrearranged and rearranged ions. However, when ions were generated by DPA rather than on electron impact, they are not significantly vibrationally excited and, hence, are less prone to undergo rearrangement. As shown above for bridgehead derivatives, the experimental ion stabilities as determined by DPA and adjusted with the appropriate leaving group correction correlate well with the stabilities calculated by *ab initio* methods (MP2/6-311G**).^{57,58} Figure 42 shows the correlation between the rate constants for solvolysis of a series of representative bridgehead bromides under standard conditions ($\log k$ for tosylate solvolysis relative to 1-adamantyl in 80% ethanol at 70°C)³⁰⁴ versus ion stabilities [$\Delta_r G^\circ(25)$].⁵⁵

The correlation in Fig. 42 is given by $\log k = 0.427\Delta_r G^\circ(25) + 0.41$ ($r^2 = 0.986$, $\sigma = 0.75$, non-bridgehead ions excluded from the correlation). It spans *ca.* 50 kcal mol^{-1} in $\Delta_r G^\circ(25)$. Conversion of $\log k$ in units of free energies of activation results in a slope of 0.67, in reasonable agreement with the slopes reported by Arnett (-0.89 in SO_2ClF , -1.02 in CH_2Cl_2 and -0.95 in SO_2). The lower value of the slope in the gas phase may be attributed to the absence of stabilization by solvent.

The bridgehead derivatives represent a mechanistically homogenous series of model compounds. Nucleophilic solvent participation (NSP) and E1 -pathways upon solvolysis are excluded for skeletal reasons, and relative rate constants are independent of leaving group and solvent. This is not necessarily so in the general case of solvolysis. DPA has now been applied to halides and alcohols leading to carbenium ions representative of various classes, such as secondary aliphatic, strained bicyclic, homoaromatic, benzyl- and cyclopropyl-stabilized ions. The relative ion stabilities are reported in Table 4. The rate constants for solvolysis of the respective halides, *p*-toluenesulfonates or *p*-nitrobenzoates are available in the literature. For reasons of consistency with the plot shown in Fig. 42, they are extrapolated to 70°C and expressed relative to 1-adamantyl solvolysis under the same conditions, assuming relative rates to be independent of leaving groups and solvent, as in the bridgehead series. These assumptions are not always justified, however. For example, significant variations in the relative rates in different solvents occur in the case of benzylic derivatives, but no systematic study was undertaken in

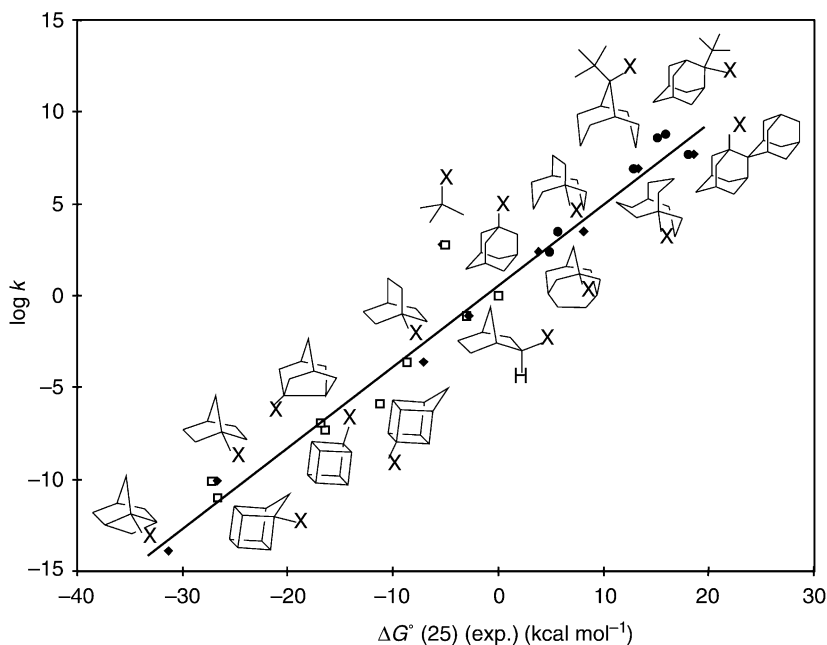


Fig. 42 Plot of $\log k$ for bridgehead derivatives versus $\Delta_r G^\circ(25)$ ($X = \text{Br}$), open squares, $\Delta_r G^\circ(29)$ ($X = \text{Br}$, calculated Cl), diamonds, and $\Delta_r G^\circ(25)$ ($X = \text{Br}$, calculated OH), filled circles.

order to determine which data are most representative. In order to minimize complications owing to NSP, rate constants for acetolysis were used in preference to data from other solvent systems. Details will be reported in a forthcoming publication.³⁰⁵

As indicated earlier, the experimental or computed gas-phase data were subject whenever necessary to the appropriate leaving correction in order to generate a homogeneous set of Gibbs energy changes based on chloride exchange, $\Delta_r G^\circ(25)$ (summarized in Table 4). For some non-bridgehead derivatives, specific leaving group corrections for *p*-toluenesulfonates were applied in order to compare exactly the same systems in the gas phase and in solution.¹⁹¹

In Fig. 43, $\log k$ for 24 substrates versus the appropriate $\Delta_r G^\circ(25)$ values are represented. A subset of 18 substrates follow the correlation equation $\log k = 0.422\Delta_r G^\circ(25) + 0.50$ ($r^2 = 0.9686$, $\sigma = 0.97$). This correlation spans over 50 kcal mol⁻¹ in $\Delta_r G^\circ(25)$. Most important is the fact that the slope is practically identical to that found for bridgehead derivatives (Fig. 42), while the quality of the fit is also excellent. While consistent behavior of bridgehead and bicyclic secondary derivatives such as 7-norbornyl (**24**), 2-adamantyl (**29**), or 4-homoadamantyl (**32**) upon solvolysis might be expected on the grounds of structural similarities and the absence of NSP, that of the other compounds of this series is surprising. The stability

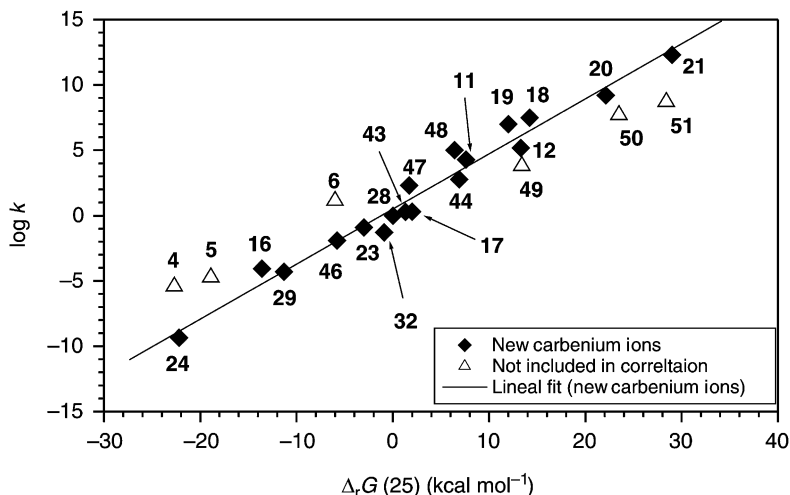


Fig. 43 $\log k$ for 24 substrates relative to 1-adamantyl chloride (computed as tosylates in 80% ethanol at 70°C), versus $\Delta_r G^\circ(25)$.

of the bicyclic secondary ions is mainly determined by strain effects. The 2-norbornyl cation (**23**) is stabilized by σ -participation, and the 7-norbornenyl (**43**) and 7-norbornadienyl (**44**) cations are homoaromatic and bishomoaromatic, respectively. In the cyclopropylcarbanyl cations **17–21** stabilization occurs through the Walsh orbitals of the cyclopropane rings, while the phenyl-substituted cations **46–51** profit from resonance stabilization. Despite these different causes for ion stability, the correlation suggests ion stability as by far the predominant factor determining solvolytic reactivity of secondary and tertiary derivatives. At the same time, the correlation confirms the qualitative concepts of strain and anchimeric participation, which have been developed over the years in the context of solvolysis.

Out of the 24 compounds represented in Fig. 43, there are six which fall outside the correlation. The low rate of triphenylmethyl chloride (**51**) in comparison to that of diphenylmethyl (**49**) or 1,1-diphenylethyl chloride (**50**) has been known for more than 35 years³⁰⁶ but, to our knowledge, has not been rationalized. However, if $\log k$ is correlated with the pK_{R^+} values of the corresponding alcohols in condensed phase, the corresponding cations, **49–51**, are well behaved (exactly as discussed in the previous section), so that their deviations in Fig. 43 must be attributed to a solvation effect. The deviations observed with the 2-propyl (**4**), 2-butyl (**5**), and *tert*-butyl (**6**) derivatives are more significant. The rate constants for these compounds, and also that of cyclopentyl (**16**) refer to tosylate acetolysis and are corrected for NSP.³⁰³ This NSP correction brings **16** on to the correlation line, but the other compounds react still significantly faster than predicted on the grounds of the stability of the respective carbenium ions. According to the definition used here,³⁰³ NSP is defined as the rate enhancement experienced by a substrate, relative to 1-adamantyl, upon

solvent change from trifluoroacetic acid to the solvent of interest. Solvents other than trifluoroacetic acid may be used as reference, but this does not fundamentally change the problem. NSP occurs in solvolysis reactions that lead to small, undelocalized carbenium ions. As shown by Takeuchi and colleagues⁶⁸ for tertiary solvolysis, NSP vanishes upon an increase of steric crowding around the reaction center, and upon increased stabilization of the positive charge by alkyl substitution. Even in the most limiting solvent HFIP, *tert*-butyl derivatives react still significantly faster than predicted on the grounds of the stability of the *tert*-butyl cation. In other words, NSP alone does not account for the total of the rate enhancement of *tert*-butyl derivatives, and the same phenomenon occurs with 2-propyl and 2-butyl. Although the transition state for solvolysis is close to the carbenium ion with respect to structure and energy, less charge is developed owing to the proximity of the leaving group and also to solvation. Apparently, these stabilizing effects are more important in the case of reactions leading to small ions such as 2-propyl or *tert*-butyl where charge is strongly localized, than to larger ions, where charge may be dispersed over a large number of atoms. For this reason, Arnett's heats of ionization of halides in the condensed phase are a more realistic model for the solvolysis reaction than is ion stability in the gas phase because they contain contributions for solvation and, although to some unknown degree, stabilization by the counter-ion.²⁹⁰ However, as Figs. 42 and 43 show, for ions having a sufficiently large number of atoms, the gas-phase stability of the carbenium ions is reflected to the same degree in the transition state for solvolysis over a very large range of reactivities, and the discrepancies between ion stabilities as determined in solution and in the gas phase are of minor significance considering the overall consistency of the data over the large range of ion stabilities.

7 Conclusion

This "low resolution" overview of the gas-phase stabilities of a variety of carbenium ions shows that they are by no means exotic data unrelated to solution reactivity. Quite on the contrary, they are the fundamental factor determining the relative stabilities of the same species in solution (as determined by the pK_R and pK_a scales, for example). Furthermore, the ranking of solvolysis rates of compounds $R-X$ is largely dependent on the intrinsic stability of R^+ . While this was already known in the case of bridgehead carbocations, we see now that this applies also to non-bridgehead tertiary cations as well as to a variety of secondary cations, even sometimes in cases wherein the access of solvent to the reaction center is not hindered. Intrinsic stability of carbocations thus appears as a very powerful unifying factor.

A number of significant problems obviously remains to be solved:

- (1) It seems highly desirable to extend both the accuracy and the size of the data base. This implies the need for more and more accurate *experimental* data.

- (2) The very existence of a remarkably simple and extensive relationship between thermodynamic and kinetic reactivity in solution and intrinsic stability is intriguing, on account of the variety of stabilities, structures and exposures to solvent involved. This raises important questions about, *inter alia*, the role of C–H...solvent hydrogen bonding interactions of carbocations in solution as well as charge delocalization effects within hydrocarbon frameworks of the carbocations.
- (3) The recent development of important quantitative empirical treatments of electrophilicity–nucleophilicity in solution^{307,308} calls for an investigation of the relationship between intrinsic stability and solution electrophilicity.

Acknowledgments

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