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Comprehensive Study of the Methyl Effect on the Solvolysis Rates of Bridgehead Derivatives

Antonio García Martínez,*,† Enrique Teso Vilar,‡ José Osío Barcina,† and Santiago de la Moya Cerero†

Contribution from the Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria, 28040 Madrid, Spain, and Departamento de Química Orgánica y Biología, Facultad de Ciencias, Universidad Nacional de Educación a Distancia (UNED), Senda del Rey 9, 28040 Madrid, Spain

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Abstract: The effect of a bridgehead methyl group on the hydride ion affinity in the gas phase of bicyclo-[1.1.1]pent-1-yl (**1**(+)), 1-norbornyl (**3**(+)), cubyl (**5**(+)), 1-adamantyl (**7**(+)), bicyclo[2.2.2]oct-1-yl (**9**(+)), and bicyclo[3.1.1]hept-1-yl (**11**(+)) cations has been studied using density functional theory and ab initio methods. It is concluded that the methyl group always increases the stability of the substituted cations. The effect of the solvent on the stability of methyl-substituted cations in relation to the unsubstituted cations has been studied using the polarizable continuum model of the self-consistent reaction field theory. In the case of rearranging cations, the nucleophilic assistance of the solvent is determined by means of the interaction energy of the corresponding water complexes. It is concluded that the solvent causes the relative stabilization of the parent cations. As a consequence, most of the methyl-substituted bridgehead derivatives show a lower solvolysis rate than the corresponding unsubstituted compounds. A nonqualitative explanation of the methyl effect on the relative stability of bridgehead cations in both gas phase and solution is given for the first time. The ratios of solvolysis products in the case of rearranging bridgehead cations have also been computed from the relative stability of the intermediate water complexes.

Introduction

Bridgehead carbocations continue being an area of interest in physical organic chemistry after several decades of study.[1] Despite the large amount of information collected, some aspects regarding the effect of the methyl group on the stability of bridgehead cations remain unexplained.[1]

In a preliminary communication[2] we have shown that the solvolysis of 4-methyl-1-norbornyl triflate (**4**(OTf)) in 60% ethanol takes place 3.74 times faster than the solvolysis of 1-norbornyl triflate (**3**(OTf)) (Figure 1). We attributed this weak accelerating effect to enhanced σ-participation. However, ab initio (MP2/6-31G*) molecular orbital calculations on the corresponding cations **3**(+) and **4**(+), carried out by other authors,[3] have been interpreted in the sense that the weak accelerating effect of the 4-methyl group is more likely a manifestation of dominant destabilizing ground-state effects.

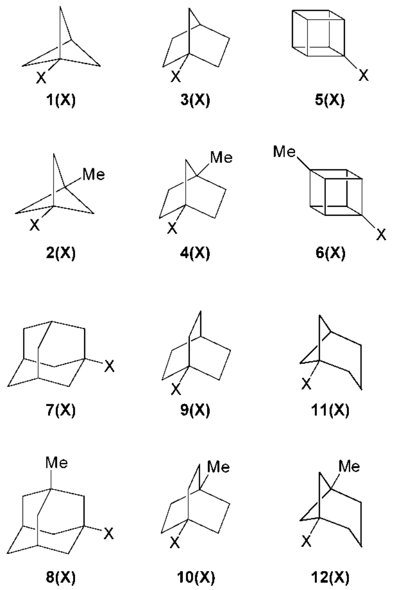

Figure 1. Studied bridgehead structures (X = +, H, or nucleofuge).

Doubts about σ-participation as basis for the striking rate enhancing effect of the methyl group in **4**(OTf) are justified because it stands in contrast to the decelerating effect of bridgehead methyl substitution in the solvolysis of all the other bridgehead derivatives studied up to now. Thus, the parent compounds bicyclo[1.1.1]pent-1-yl bromide (**1**(Br)),[4] cubyl triflate (**5**(OTf)),[5] 1-adamantyl bromide (**7**(Br)),[6] bicyclo[2.2.2]-

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* Corresponding author. Phone: +91 3944333. Fax: +91 3944103. E-mail: josio@quim.ucm.es.
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‡ Universidad Nacional de Educación a Distancia (UNED).

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Table 1. Experimental Rate-Constant Ratios (k_{Me}/k_H)

structures		solvolysis conditions			
"H" (non-methyl-substituted)	"Me" (methyl-substituted)	solvent	T (°C)	k_{Me}/k_H	ref.
1(I)	**2**(I)	80% EtOH	45	5.5×10^2	4
1(Br)	**2**(Br)	80% EtOH	70	5.2×10^2	4
3(OTf)	**4**(OTf)	80% EtOH	80	3.91	3
		97% TFE	60	7.41	3
5(OTf)	**6**(OTf)	MeOH	50	0.53	5
7(Br)	**8**(Br)	AcOH	75	0.71	6
9(OBs)	**10**(OBs)	AcOH	70	0.30	6
9(ONs)	**10**(ONs)	80% EtOH	70	2.22×10^2	7
11(Br)	**12**(Br)	80% EtOH	70	0.04	8

oct-1-yl brosylate (**9**(OBs)),[6,7] and bicyclo[3.1.1]hept-1-yl bromide (**11**(Br))[8] have been found to solvolyze faster than the corresponding bridgehead methyl-substituted derivatives **2**(Br), **6**(OTf), **8**(Br), **10**(OBs), and **12**(Br), respectively. The relative solvolysis rates k_{Me}/k_H are given in Table 1. Moreover, it has been known for some time that the successive introduction of methyl groups at the bridgehead positions C-3, C-5, and C-7 of **7**(Br) reduces the solvolysis rate by a factor of ca.1.47 per methyl group.[9]

Usually, the rate depressions caused by the methyl group have been attributed to its σ-acceptor effect as measured by the inductive constant $\sigma_I{}^q = 0.11$,[10] since there is a good linear correlation between log k of the solvolysis of bridgehead substituted compounds of the types **2**,[4] **8**,[6,7] **10**,[6,7] and **12** [8] with the $\sigma_I{}^q$ value of the corresponding polar substituents. For the **4** [3] and **6** [5] systems the available data are so limited that a meaningful correlation is not attainable.

On the other hand, the fact that a methyl group at C-4 position depresses the rate of solvolysis of cubyl triflate **5**(OTf) has been taken as evidence against charge delocalization at this position.[5c] The hyperconjugative stabilization by the methyl group (π-effect) has been considered ineffective in cation **6**(+) by the off-axis positioning of the methyl C−H bonds relative to the symmetry axis of the cation LUMO.[5c,11a] Nevertheless, it should be taken into account that there is also a good linear correlation between log k of bridgehead substituted compounds of type **2**,[12] **8**,[6] and **10** [6] and the inductive effect of the substituents measured by the σ_I-scale, in which the methyl group ($\sigma_I = -0.01$) is electron releasing.[13] Thus, definitive conclusions regarding the direction of the inductive effect of a methyl group relative to hydrogen cannot be reached from the present solvolysis data. A striking feature of the correlations between log k and inductive effects is that the points for the parent compounds **1**,[4] **9**,[6,7] and **11** [8] lie significantly above the regression line. This unusual stabilizing effect of hydrogen has been formerly attributed to a structural change upon replacing it by a methyl group.[3,6] A more recent study of the solvolysis of **1(**Br**)**[12] has suggested that the exalted solvolysis rate in nucleophilic solvents should be due to solvation of the cationic transition state at 3-H. Hence, the rate depression caused by the introduction of a methyl group at the bridgehead position should be attributed to a poor hydrogen bonding stabilization of the corresponding cations.[7,11]

On the other hand, significant secondary deuterium isotope effects have been measured for the **1**(X),[12] **7**(X),[14] **9**(X),[15] and **11**(X)[8a] systems. These isotope effects have been interpreted as a probe of participation of the bridgehead C−H bond in the stabilization of the corresponding cations. In our opinion, this explanation is not conclusive since the isotope effect could be also due to changes in the C−H(D) force constant promoted by hybridization changes resulting from strain increase during the ionization step (vide infra).[8d] To provide a conclusive answer to the striking question of the methyl effect, we have sought recourse to density functional theory (DFT) and ab initio molecular orbital computations on the cations and hydrocarbons **1**−**12** in gas phase as well as in solution using the polarizable continuum model (PCM) method of the self-consistent reaction field (SCRF) theory.

Results and Discussion

Computations in the Gas Phase. The inclusion of polarization functions and electron correlation has proved to be essential for the reliable calculation of carbocation energies.[11] Thus, there is a good correlation between the differences in total energy (ΔE) between bridgehead cations and the corresponding hydrocarbons (ΔE[R(+)−R(H)]) calculated with the ab initio Möller−Plesset MP2/6-31G* method and log k.[3,11] Recently it has been shown that log k (in 80% EtOH) of unsubstituted bridgehead derivatives correlate with the gas-phase stability determined with the experimental dissociative proton attachment (DPA) method as well as with the computed with the MP2/6-311G** method.[17a]

The Lee−Yang−Parr (LYP) three-parameter exchange-correlation functional (B3LYP) of the DFT[18] provides significantly greater accuracy than the Hartree−Fock theory with only a small

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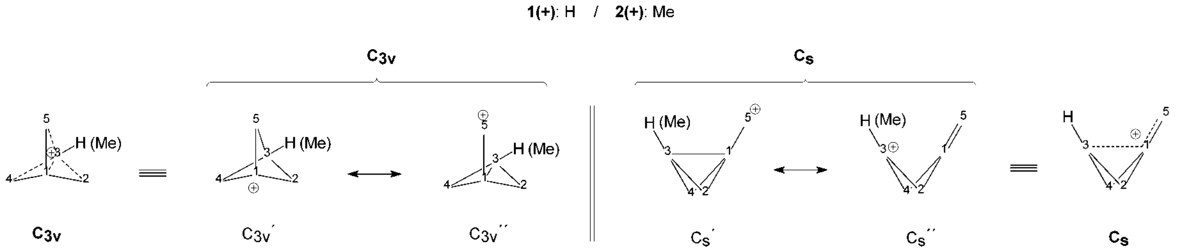
Table 2. Computed Relative Total Energies of the C_{3v} and C_s Structures [$\Delta E = E(C_{3v}) - E(C_s)$ (kcal/mol)] of Cations **1**(+) and **2**(+)



method	cation	ΔE	cation	ΔE	method	cation	ΔE	cation	ΔE
B3LYP/6-31G*	**1**(+)	*a*	**2**(+)	*a*	MP2(full)/6-31G*	**1**(+)	6.90[b]	**2**(+)	11.36[b]
B3LYP/6-311G**		13.69		20.02	MP2(full)/6-311G**		5.92		9.68

[a] Converges to the C_s structure. [b] Computed geometry and energy agree with previously reported data (see ref 22b). The structure of **1**(+)[C_{3v}] was incorrectly described in ref 22b as a **1**(+)[C_s]-like geometry.

increase in CPU time and disk usage, because it includes some of the effects of electronic correlation. However, apart from us,[19] this functional has not been employed for the study of bridgehead cations. We now report the calculation of the energies of cations **1**(+)−**12**(+) and the corresponding hydrocarbons **1**(H)−**12**(H) with the B3LYP functional and the standard basis set 6-31G* implemented in the GAUSSIAN 98W package.[20] In the case of **3**(H), **3**(+), **4**(H), **4**(+), **10**(H), and **10**(+), computations with the B3LYP/6-31+G**//B3LYP/6-31G* method have also been carried out. On the other hand, the structures **1**(H), **1**(+), **2**(H), and **2**(+) have been studied using the basis sets 6-31G* and 6-311G** at the B3LYP as well as at the ab initio MP2(full) theoretical levels.[20]

The geometries and total energies of carbocations and hydrocarbons **1**−**12** (E[R(+)] and E[R(H)], respectively) have been fully optimized with the B3LYP/6-31G* method using standard gradient-optimization techniques.[20] The computed total energies (E) are not corrected by zero-point vibrational energy (ZPVE). The Gibbs free energies (G) have been computed from harmonic vibrational frequency calculations with the B3LYP/6-31G* method using analytic second derivative procedures.[20] No imaginary frequencies have been found (see later for the case of **1**(+) and **2**(+) and ref 2 for **3**(+)), showing that the computed structures for both hydrocarbons and cations of types **1**−**12** correspond to energy minima. The atomic charges have been computed from Mulliken population analysis on the calculated wave functions in each case.[20] Population analysis of **1**(+) cation has been performed using the atoms in molecules (AIM)[21] procedure as well as the Mulliken method.[22a] The atomic charges from both population analyses are different but show the same trend and lead to the same conclusions concerning the changes in charge on going from the hydrocarbon to the cation.[22a] We have attempted to compute the charges of cations **3**(+), **9**(+), and **10**(+) using the AIM method, but no convergence was achieved. Unfortunately, this method usually fails in the case of cage molecules with atoms with very curved surfaces, because the atomic surface sheet cannot be determined in the Newton−Raphson step.[20]

The geometries computed by us for hydrocarbons and cations **3**−**5** and **9** with the B3LYP/6-31G* method are in agreement with the reported structures for **3**,[3] **4**,[3] and **9** [23] with the MP2-(full)/6-31G* method as well as with that computed for **5** using the MP2(full)/6-31G** method.[24]

Question of the Structure of Cations 1(+) and 2(+). There is some uncertainty regarding the structures of bicyclo[1.1.1]-pent-1-yl cations **1**(+) and **2**(+). For cation **1**(+), a C_{3v} geometry (analogous to **1**(+)[C_{3v}] in Table 2) has been previously proposed as a stable structure using the MP2/6-31G** method.[24] A calculation of the vibrational frequencies for **1**(+)-[C_{3v}] with the MP4/6-31G* and MP2(full)/6-31G* methods found one degenerate imaginary frequency, indicating it to be a transition state.[22] The imaginary mode was followed down to the first intermediate, which was found to be the bicyclo[1.1.0]-but-1-ylcarbinyl cation with C_s symmetry **1**(+)[C_s] (Table 2).[22] By contrast, all of the frequencies of the 3-methyl-substituted cation **2**(+) with C_{3v} symmetry (**2**(+)[C_{3v}]) (Table 2) computed with the HF/6-31G* method were real.[22] The energy of **2**(+)-[C_{3v}] has also been calculated at the MP4 and MP2(full) levels with the 6-31G* basis set.[22]

We have computed the structure and energy of cations **1**(+) and **2**(+) and the corresponding hydrocarbons **1**(H) and **2**(H) with the B3LYP/6-31G*, B3LYP/6-311G**, MP2(full)/6-31G* and MP2(full)/6-311G** methods. The computed relative energies ΔE are given in Table 2. The E values computed by us with the MP2(full)/6-31G* method are identical to those previously reported in the literature.[22] The C_{3v} geometry of both cations computed with the B3LYP/6-31G* method is not a stationary point. Thus, the energy optimization of both cations affords the corresponding C_s structures **1**(+)[C_s] and **2**(+)[C_s]. Contrary to the B3LYP/6-31G* method, the C_{3v} structures computed with the B3LYP/6-311G**, MP2(full)/6-31G* [22] and

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MP2(full)/6-311G** methods for the **1**(+)[C_{3v}] and **2**(+)[C_{3v}] cations are stationary points, but no global minimum energy structures.

The geometries computed by us with the four methods are very similar, but not the corresponding charge distributions. The C_s structures of **1**(+) and **2**(+) can be described as resonance hybrids between the canonical structures C_s' and C_s'' (Table 2), considering the short $R(1,5)$ and large $R(1,3)$ distances (1.348 vs 1.641 Å for **1**(+)[C_s] and 1.341 vs 1.730 Å for **2**(+)[C_s], computed with the B3LYP/6-311G** method). The C_s' structure is like a bicyclo[1.1.0]but-1-ylcarbinyl cation,[22] whereas C_s'' is like a puckered 3-methylenecyclobutyl cation (angle of pucker ca. 45°). This last structure is more stable than the classical 3-methylenecyclobutyl cation previously discussed in the literature.[22b,25]

The charge distribution of the C_{3v} cations as well as the short carbon−carbon distances $R(1,3)$ and large $R(3,5)$ distances (1.535 and 1.609 Å for **1**(+) as well as 1.551 and 1.625 Å for **2**(+), computed with the B3LYP/6-311G** method) suggest that these cations are indeed resonance hybrids between the canonical structures C_{3v}' and C_{3v}'' (and symmetry related structures, Table 2; for other canonical contributors, see later).[24]

On the other hand, it has been previously shown, according to the HF/6-31G* method, that the bridgehead methyl group causes a stabilization of the C_{3v} structure of **2**(+) in relation to the corresponding C_s structure.[22b] Unlike these results, our computations using the B3LYP/6-311G** and MP2(full)/6-311G** methods show that the methyl group causes the stabilization of the C_s structure by 6.3 or 3.8 kcal/mol, respectively, in relation to the corresponding C_{3v} structure (calculated from the ΔE values in Table 2).

Structures of Cations 11(+) and 12(+). We have included in this paper the study of the methyl effect on the stability of cation **11**(+) by the kind suggestion of a reviewer. Compound **11**(Br) solvolyzes in methanol at a surprisingly high rate, because it is seven times more reactive than *tert*-butyl bromide.[8a,26] This substrate undergoes solvolysis even 3.5 times faster than **1**(Br).[27] The enhanced solvolysis rates have been attributed to stabilization of cation **11**(+) by through-space interactions as well as homohyperconjugation.[8a]

We have optimized the structures of cations **11**(+) and **12**(+) and computed the corresponding energies using the B3LYP/6-31G* method. Our results show that cations **11**(+) and **12**(+) are σ-bridged structures, which can be described as resonance hybrids between the C_1', C_1'', and C_1''' structures (Figure 2). The computed structures for both **11**(+) and **12**(+) support the through-space bonding interaction between the bridgehead carbon atoms, as shown by the participation of the canonical contributor C_1''', and, hence, a short $R(1,5)$ distance (1.855 Å for **11** and 2.039 for **12**). However, there is no geometrical data supporting the claimed homohyperconjugative stabilization, because the $R(5,\text{H})$ distance in cation **11**(+) is even shorter than in the corresponding hydrocarbon **11**(H) (1.088 Å vs 1.096 Å). We think that the corresponding change in the C−H(D) force constant is the correct explanation of the isotope effect (vide supra).

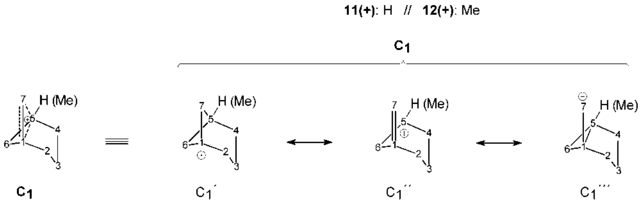

Figure 2. Canonical contributors to the structures of cations **11**(+) and **12**(+).

The introduction of a methyl group at C-5 leads to a retardation of solvolysis[8] (Table 1). The exalted rate of the parent bromide **11**(Br) was ascribed to solvation of the bridgehead C−H bond.[8] Strikingly, our computed hydride affinities show that the methyl-substituted cation **12**(+) is more stable than the parent cation **11**(+) (vide infra). In this context, it is even more surprising that the through-space orbital interaction is smaller in the case of **12**(+). Thus, the $R(1,5)$ distance of **12**(+) is larger than that computed for **11**(+) (vide supra).

The σ-bridged (nonclassical) cation **11**(+) shown in Figure 2 is more stable (by 8.9 kcal/mol, the B3LYP/6-31G* method) than the classical 3-methylenecyclohexyl cation. We decided not to compute the corresponding ΔE value by using the MP2(full)/6-31G* method because the classical cation was not stable (!) under the MP2(full) Hamiltonian. Thus, the optimization of the classical cation leads to the 2-methylenecyclohexyl cation, formed by 1,2-hydride shift.

Nature of the Methyl Effect in the Gas Phase. The stability of a cation is inverse to its hydride affinity as given by $\Delta E[\text{R}(+)-\text{R}(\text{H})]$, i.e. the difference in total energies between the cation R(+) and the parent hydrocarbon R(H).[3,11,16,19,28] The $\Delta E[\text{R}(+)-\text{R}(\text{H})]$ values calculated by us using the B3LYP/6-31G* method are given in Table 3. The data listed reveal that a bridgehead methyl substituent always has the effect of reducing the energy required for the formation of the cation relative to the unsubstituted hydrocarbon. The stabilizing effect (methyl effect) is given by $\Delta\Delta E[\text{R}(+)-\text{R}(\text{H})]$ ($\Delta\Delta E$ in Table 3), i.e. the difference in hydride affinities between the substituted ("Me" in Table 3) and unsubstituted ("H" in Table 3) cations. The $\Delta\Delta E$ values have the status of the heat of the isodesmic reaction:

$$\text{R}_\text{H}(+) + \text{R}_\text{Me}(\text{H}) \rightarrow \text{R}_\text{H}(\text{H}) + \text{R}_\text{Me}(+) + \Delta\Delta E$$

involving cations (+) and hydrocarbons (H) of the unsubstituted (R_H) and methyl-substituted (R_Me) substrates. In all cases the methyl effect is negative; i.e. the bridgehead methyl group causes the stabilization of the corresponding cations.

In the case of the cations **1**(+) and **2**(+), the methyl effect is depending on their C_{3v} or C_s symmetry as well as the computational method, particularly in the case of the C_s cations (Table 3). The transannular bonding orbital interaction (through-

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(25) In the opinion of one of the reviewers, the B3LYP method is known to overestimate the stabilization energies of delocalized structures. However, this fact is not manifested in the case of bridgehead cations. Thus, as shown in eq 1, there is an excellent relationship between cation energies (without correction) using the B3LYP/ and MP2(full)/6-31G* methods. In the case of cations **1**(+), the difference in energy (ΔE) between the classical 3-methylenecyclobutyl cation and the nonclassical **1**(+)[C_s] structures is 12.6 kcal/mol, calculated by us with the B3LYP/6-31G* method, but even higher, 16.6 kcal/mol using the MP2(full)/6-31G* method.[22b]

(26) Della, E. W.; Pigou, P. E.; Tsanaktsidis, J. *J. Chem. Soc., Chem. Commun.* **1987**, 833.

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Table 3. B3LYP/6-31G*-, B3LYP/6-311G**-, MP2(full)/6-31G*- and MP2(full)/6-311G**-Calculated Hydride Affinities of Carbocations in Both Gas Phase ($\Delta E[\mathrm{R}(+)-\mathrm{R(H)}]$) and Solution ($\Delta G^{\mathrm{sol}}[\mathrm{R}(+)-\mathrm{R[H]}]$) (kcal/mol): Calculated Methyl Effects in Both Gas Phase ($\Delta\Delta E$) and Solution ($\Delta\Delta G^{\mathrm{sol}}$) and Deviation from Experimental Data (δG^{sol})

structures initial hydrocarbon → carbocatio n		computed data							exptl data		
			ΔE[R(+) – R(H)]			ΔG^{sol}[R(+) R(H)][a]					
"H" (non-methyl-substituted)	"Me" (methyl-substituted)	method	"H"	"Me"	$\Delta\Delta E$	"H"	"Me"	$\Delta\Delta G^{\mathrm{sol}}$	$k_{\mathrm{Me}}/k_{\mathrm{H}}$[b]	$\Delta\Delta G_{\mathrm{exp}}^{\mathrm{sol}}$	δG^{sol}
1(H) → **1**(+)[C_{3v}]	**2**(H) → **2**(+)[C_{3v}]	B3LYP/6- 311G**	574.2	571.6	−2.6	518.7	521.2	2.5	5.5×10^{-2} [5.2×10^{-2}]	2.0 [2.3]	0.5 [0.8]
		MP2(full)/ 6-31G*	552.4	549.9	−2.5	486.0	488.6	2.6			0.6 [0.3]
		MP2(full)/ 6-311G**	565.8	563.0	−2.8	587.8	590.1	2.3			0.3 [0.0]
1(H) → **1**(+)[C_s]	**2**(H) → **2**(+)[C_s]	B3LYP/6- 31G*	557.4	548.6	−8.8	506.7	502.5	−4.2			−6.2 [−6.5]
		B3LYP/6- 311G**	562.7	551.6	−1.1	478.1	475.5	−2.6			−4.6 [−4.9]
		MP2(full)/ 6-31G*	545.5	538.9	−6.6	509.8	505.4	−4.4			−6.4 [−6.7]
		MP2(full)/ 6-311G**	559.9	553.0	−6.9	479.7	476.4	−3.3			−5.3 [−5.6]
3(H) → **3**(+)	**4**(H) → **4**(+)	B3LYP/6- 31G*	582.1	578.6	−3.5	529.8	528.5	−1.3	3.91	−1.0	−0.3
						530.3	529.1	−1.2	7.41	−1.5	0.3
5(H) → **5**(+)	**6**(H) → **6**(+)	B3LYP/6- 31G*	577.1	575.3	−1.8	521.8	521.4	−0.4	0.53	0.4	−0.8
7(H) → **7**(+)	**8**(H) → **8**(+)	B3LYP/6- 31G*	556.7	555.4	−1.3	509.7	510.5	0.8	0.71	0.2	0.6
9(H) → **9**(+)	**10**(H) → **10**(+)	B3LYP/6- 31G*	565.5	565.2	−0.2	529.2	530.1	0.8	0.30	1.4	−0.6
						515.6	516.6	0.9	2.22×10^{-2}	3.0	−2.1
11(H) → **11**(+)	**12**(H) → **12**(+)	B3LYP/6- 31G*	556.3	549.6	−6.7	508.4	504.2	−4.2	0.04	2.6	−6.8

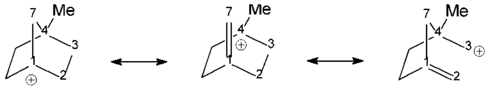
[a] Computed using both temperature and ϵ-value corresponding to the experimental condition in which each $k_{\mathrm{Me}}/k_{\mathrm{H}}$ ratio was measured (see Table 1). [b] From Table 1 (different reported $k_{\mathrm{Me}}/k_{\mathrm{H}}$ for the same structure type and solvolysis conditions but with a different nucleofuge are distinguished into square brackets).

space effect) in **2**(+)[C_{3v}] is higher than in the case of **2**(+)-[C_s] in accord with the corresponding R(1,3) distances (1.551 vs 1.730 Å, computed with the B3LYP/6-311G*method). The through-space interaction causes the decrease of the interaction between C-3 and the methyl group in the case of **2**(+)[C_{3v}]. This fact is reflected not only in the lower methyl effect ($\Delta\Delta E$ values, Table 3) but also in the R(3,CH_3) distances: 1.528 Å in **2**(+)[C_{3v}] vs 1.470 Å in **2**(+)[C_s] (B3LYP/6-311G* values). The through-space interaction is also the reason for the high $\Delta\Delta E$ value computed in the case of cations **11**(+) and **12**(+) with the B3LYP/6-31G* method (Table 3).

To evaluate the effect of increasing the flexibility of the basis set on the methyl effect in the case of non-rearranging bridgehead cations, B3LYP/6-31+G** total energies for the substrates **3** and **4** have been computed by us starting from the B3LYP/6-31G* geometries (B3LYP/6-31+G**//B3LYP/6-31G* method). The resulting methyl effect is now $\Delta\Delta E = -3.4$ kcal/mol, very similar to the calculated with the B3LYP/6-31G* method (−3.5 kcal/mol, Table 3).

In our opinion, the generality of the cation stabilizing methyl effect is most probably due to a common electronic factor (σ-delocalization and inductive effect) enhanced by the methyl group rather than to specific destabilization of the parent hydrocarbons. To gain information on the electronic nature of the methyl effect, it seems convenient to examine the effect of the substitution of hydrogen by a methyl group on the charge distribution and geometry of bridgehead cations and the corresponding hydrocarbons.

Only charge distributions of the cations and hydrocarbons of types **1**,[22,24] **3**,[3,19] **4**,[3] **5**,[11,24] **7**,[19] and **9** [29] have been computed and discussed in the literature up to now. We have computed the charge distributions from Mulliken population analysis (vide supra) using the B3LYP/6-31G* method for cations and hydrocarbons **1**−**12** and found that the methyl group is electron withdrawing in the case of the hydrocarbons[16,21] but electron releasing in the case of the corresponding cations. Thus, for example, in the case of the norbornane system the charge at the bridgehead carbon C-1 in **3**(H) is +0.016 au, but +0.104 au (at the equivalent position) in the case of **4**(H). On the other hand, the charge +0.074 au at C-4 of **3**(+) decreases to +0.036 au in **4**(+). The general electron-releasing effect of a methyl group in the case of bridgehead cations is clearly due to the higher electron demand caused by the ionization.[19]



4(+)′ **4(+)′′** **4(+)′′′**

Figure 3. Canonical contributors to structure of carbocation **4**(+).

The general stabilizing electronic effect of the methyl group in the case of the bridgehead cations is not only inductive (stabilizing polarizability effect of the methyl group relative to hydrogen) but also hyperconjugative because the introduction of a methyl group generates significant bond length changes in both hydrocarbons and cations. Thus, for instance, in the case of cation **4**(+) the bond length changes of the methano bridge are noteworthy. In terms of the valence bond theory, the hyperconjugative effect of the methyl group causes the enhanced contribution of the canonical structure **4**(+)″ (Figure 3). Thus, the lengthening of the C-4−C-7 bond and the shortening of the C-7−C-1 bond in going from the hydrocarbon to the cation are larger than in the case of cation **3**(+) (R(4,7) = 1.593 Å and R(1,7) = 1.480 Å in **3**(+) vs 1.613 and 1.469 Å in **4**(+)). On the other hand, the contribution of structure **4**(+)‴ (Figure 3) is similar in both cations **3**(+) and **4**(+), because the C-2−C-3 bond changes are also similar in both cases (R(2,3) = 1.611 Å in **3**(+) vs 1.606 Å in **4**(+)). Besides this, the canonical structure **4**(+)″ is analogous to a canonical structure proposed as contributor to the overall structure of **1**(+)[C_{3v}].[22,24]

The comments of one of the reviewers have prompted us to study the reasons of the stabilizing effect of the methyl group in cations **6**(+) and **10**(+). The structure of the unsubstituted cation **9**(+) is stabilized by through-bond coupling (double hyperconjugation).[15] Our computations confirm the participation of the canonical structure **9**(+)″ (and symmetry related ones; Figure 4) because the ionization of **9**(H) is accompanied by lengthening of the R(2,3) and shortening of the R(1,2) (1.542 vs 1.460 Å) and R(3,4) (1.542 vs 1.538 Å) distances. In the

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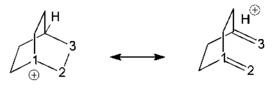
(29) Bentley, T. W.; Roberts, K. *J. Org. Chem.* **1985**, *50*, 5852.



9(+)′ **9(+)″**

Figure 4. Canonical contributors to structure of carbocation **9**(+).

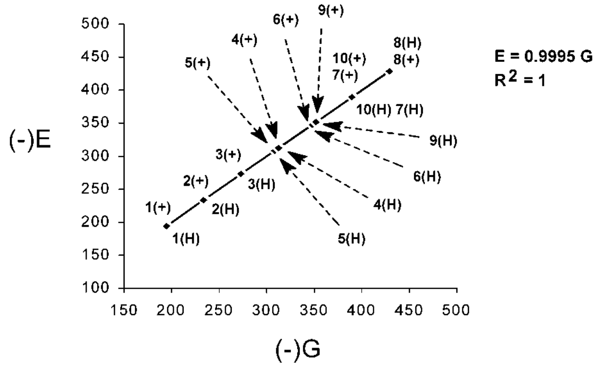


Figure 5. Linear relationship *E* vs *G* obtained from B3LYP/6-31G* (computed *E* and *G* values in hartrees).

case of the methyl substituted cation **10**(+), the through-bond coupling is not favored (the *R*(2,3) distance (1.631 Å) is even shorter than in the case of **9**(+) (1.638 Å)). This Baker−Nathan effect can be accounted for by supposing that the hyperconjugative ability of a C−C bond is smaller than that expected for a C−H bond.[30] Similar situations take place in the case of cubyl cations **5**(+) and **6**(+).

On the other hand, the π-electron donor effect of the methyl group is not effective at the C-1 position of cations **6**(+) and **10**(+) (vide supra).[5c,11a] Hence, the main reason for the stabilizing methyl effect in the case of these C_{3v} cations seems to be the electron release of the methyl group, particularly toward the ipso positions, due to the electrostatic field of the positively charged cage.

Two Noteworthy Relationships in the Gas Phase. There is an excellent correlation between the B3LYP and MP2(full) total energies of cations **1**(+)−**10**(+) computed using the same 6-31G* basis set. Thus, both *E*[R(+)] values are related by eq 1, which allows the calculation of MP2 energies from the corresponding B3LYP values, within an error of ±1.5 kcal/mol, comprising a Δ*E* range beyond 200 hartrees (!).

$$E[\mathrm{R}(+)]_{\mathrm{MP2}} = 0.9964E[\mathrm{R}(+)]_{\mathrm{B3LYP}} \qquad (1)$$

There is also a striking good relationship between the total energies *E* (without thermal and ZPVE corrections) of all hydrocarbons and cations with the corresponding sum of electronic and thermal free energies *G* (Figure 5). Thus, *G* values (at 298 K and 1 atm) can be calculated from *E* values using eq 2, obtained by linear regression analysis, within an error of ±2.2 kcal/mol.

$$G = E - 8.5 \qquad (2)$$

On the other hand, the differences in free energies between cations and hydrocarbons with ZPVE and thermal corrections (Δ*G*), can be calculated from uncorrected differences in total energies (Δ*E*) by using eq 2a within an error of ±0.5 kcal/mol (!).

$$\Delta G = \Delta E - 9.1 \qquad (2a)$$

The corresponding entropy of symmetry corrections are not needed for the calculation of Δ*G* of solvolytic reactions because no changes in the number of symmetry (σ) takes place.[17] Since $\Delta E \gg 9.1$, the approximation $\Delta G = \Delta E$ is justified in the gas phase. As a corollary, the correlation lines between Δ*G*[R(+)−R(H)] or Δ*E*[R(+)−R(H)] vs the corresponding solvolysis rates (ln *k*; Schleyer's plots) show the same slope.[19]

Despite $\Delta S = 0$, it is necessary to extrapolate rate constants to the same temperature for the Schleyer's plot, because Δ*G* is independent of the temperature only for a series of reactions at the same pressure. Thus, eq 2b, obtained by partial differentiation of eq 2a, is only valid at constant pressure and $\Delta S = 0$.

$$(\partial \Delta G/\partial T)_p = 0 \qquad (2b)$$

The solvolyzes of bridgehead derivatives are usually carried out in sealed tubes. Therefore, the constant pressure condition requires the reactions to be accomplished at the same temperature.

Nature of the Methyl Effect in Solution. It is well-accepted that 80−90% of the free energy difference in the gas phase between a bridgehead carbocation and the corresponding hydrocarbon, Δ*G*[R(+)−R(H)], is reflected in the transition state of solvolytic reactions.[28,29,32] This corresponds to a mean slope of $m = 0.85$ for the correlation line obtained by plotting a wide range of solvolysis rates (− ln *k*) of bridgehead derivatives vs Δ*G*[R(+)−R(H)] computed in the gas phase.[29,32]

From a slope of $m = 0.85$ and the experimental $k_{\mathrm{Me}}/k_{\mathrm{H}}$ rate ratios for substrates **1**−**12**, we have evaluated the experimental relative hydride affinities of the intermediate carbocations in solution, $\Delta\Delta G^{\mathrm{sol}}[\mathrm{R}(+)-\mathrm{R(H)}]_{\mathrm{exp}}$ ($\Delta\Delta G_{\mathrm{exp}}{}^{\mathrm{sol}}$ in Table 3), using eq 3.

$$\Delta\Delta G^{\mathrm{sol}}[\mathrm{R}(+)-\mathrm{R(H)}]_{\mathrm{exp}} = -1/m[RT\ln(k_{\mathrm{Me}}/k_{\mathrm{H}})] \qquad (3)$$

The resulting values are listed in Table 3. In all cases, with only the exception of the norbornyl derivatives, $\Delta\Delta G^{\mathrm{sol}}[\mathrm{R}(+)-\mathrm{R(H)}]_{\mathrm{exp}}$ values are positive, showing that the introduction of a methyl group causes the destabilization of the corresponding cations in solution in relation to the unsubstituted cations.

To understand the striking differences of the methyl effect in gas phase and in solution as measured by the ΔΔ*E*[R(+)−R(H)] and $\Delta\Delta G^{\mathrm{sol}}[\mathrm{R}(+)-\mathrm{R(H)}]_{\mathrm{exp}}$ values, respectively, we have sought to compute the free energies in solution of substrates **1**−**12**. The polarizable continuum model (PCM)[33] of the self-consistent reaction field theory (SCRF)[34] is a convenient approach for this purpose, although this model has been scarcely applied until now to the study of solvolytic reactions.[35]

The total free energies in solution (including nonelectrostatic terms) G^{sol} of the hydrocarbons **1**(H)−**12**(H) and the corre-

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(30) Grob, C. A.; Rich, R. *Tetrahedron Lett.* **1978**, 663, and references cited therein. In the opinion of one of the reviewers, the relative hyperconjugative donor abilities of the C−C and C−H bonds is a controversial question: (a) Wu, Y.-D.; Tucker, J. A.; Houck, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5018, and references cited therein. (b) Rablen, P. R.; Hoffmann, R. W.; Hrovat, D. A.; Borden, W. T. *J. Chem. Soc., Perkin Trans. 2* **1999**, *2*, 1719, and references cited therein.

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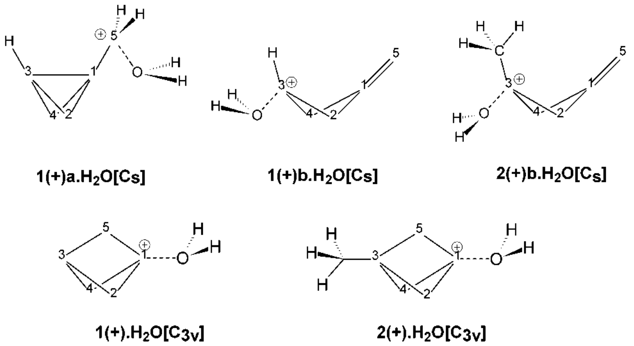
(34) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(35) (a) Ford, G. P.; Wang, B. *J. Am. Chem. Soc.* **1992**, *114*, 10563. (b) Smith, W. B. *J. Org. Chem.* **2001**, *66*, 376.

Table 4. MP2(full)/6-31G*- and B3LYP/6-311G**-Computed Water Complexes of Cations **1**(+) and **2**(+) [Relative Total Energies (Δ*E*), kcal/mol]



method	**1**(+)**a**·H₂O[*Cs*]	**1**(+)**b**·H₂O[*Cs*]	**1**(+)·H₂O[*C*₃ᵥ]	**2**(+)**b**·H₂O[*Cs*]	**2**(+)·H₂O[*C*₃ᵥ]
MP2(full)/6-31G*	10.3	0.0	9.0	0.0	11.4
B3LYP/6-311G**	10.9	0.0	17.4	0.0‘	19.7

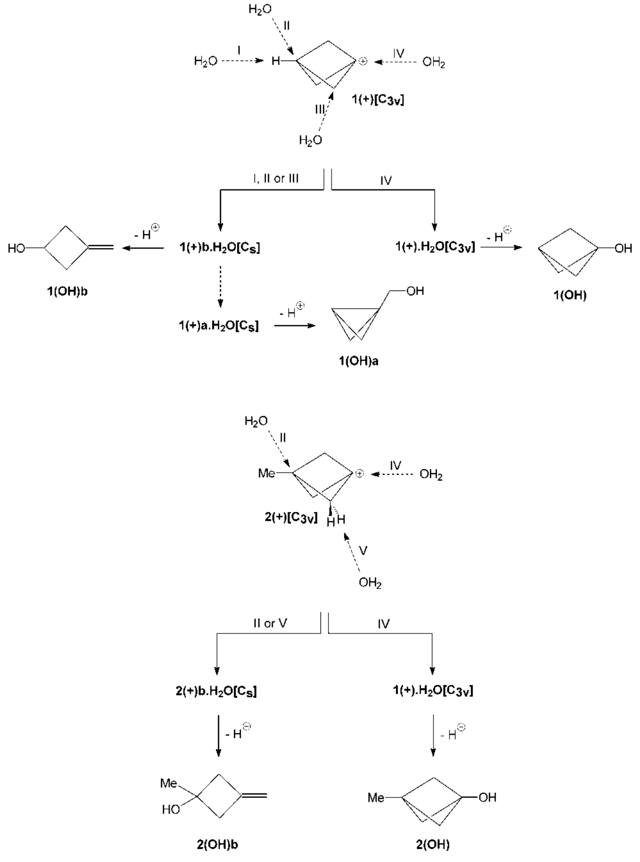
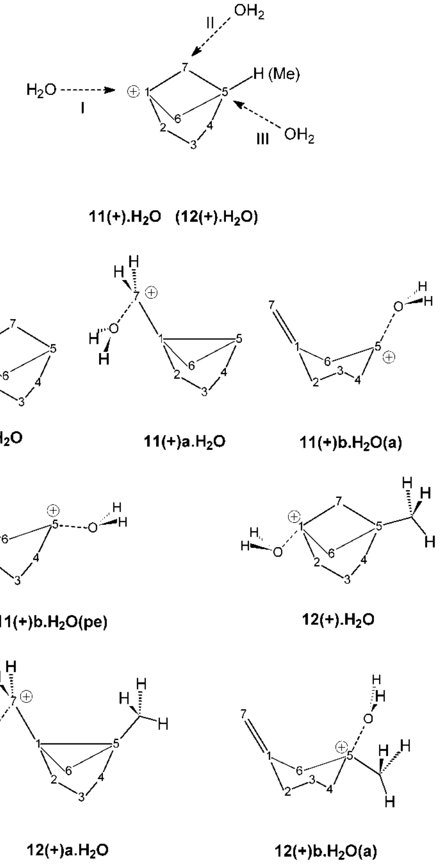


Figure 6. Predicted reaction products from nucleophilic attack of water on the corresponding MP2(full)/6-31G*-computed intermediates **1(+)[***C*$_{3v}$**]** and **2**(+)[*C*$_{3v}$].

Table 5. B3LYP/6-31G*-Computed Water Complexes of Cations **11**(+) and **12**(+) [Relative Total Energies (Δ*E*), kcal/mol]



complex	Δ*E*	complex	Δ*E*
11(+)·H₂O	10.5	**12**(+)·H₂O	14.1
11(+)**a**·H₂O	12.3	**12**(+)**a**·H₂O	12.7
11(+)**b**·H₂O(a)	0.0	**12**(+)**b**·H₂O(a)	0.0
11(+)**b**·H₂O(pe)	11.2		

sponding cations **1**(+)−**12**(+) have been computed in the actual solvent mixtures and at the temperatures of solvolysis. The computations have been performed with the PCM model implemented in GAUSSIAN 98W2.0 at the B3LYP and MP2(full) levels using the 6-31G* and 6-31G** basis sets. The cavity has been defined as the union of a series of interlocking atomic spheres (using standard *f* values), whose surface has been subdivided into 60 initial tesserae (pentakisdodecahedron). The relative hydride affinities $\Delta\Delta G^{sol}$ have been calculated from the corresponding differences in total solvation free energies ΔG^{sol}[R(+)−R(H)] and are listed in Table 3. The differences between the computed $\Delta\Delta G^{sol}$[R(+)−R(H)] and the experimental $\Delta\Delta G^{sol}$[R(+)−R(H)]$_{exp}$ methyl effects on the hydride affinity of the corresponding carbocations are given in Table 3 as δG^{sol}.

The comparison of $\Delta\Delta E$[R(+)−R(H)] values (which are equivalent to $\Delta\Delta G$; see eq 2a) with the computed $\Delta\Delta G^{sol}$[R(+)−R(H)] clearly shows that solvation causes a pronounced

Table 6. MP2(full)/6-31G*- and B3LYP/6-311G**-Calculated Water−Carbocation Interaction Energies (ΔE_w; kcal/mol): Determination of the Water-Assisted Methyl Effect in Both Gas Phase ($\Delta\Delta E_w$) and Solution ($\Delta\Delta G_w^{sol}$), and Deviation from δG^{sol} ($\delta G^{sol} - \Delta\Delta G_w^{sol}$)

structures initial hydrocarbon → more stable water–complex carbocation		computed data					
			ΔE_w[a]				
"H" (non-methyl-substituted)	"Me" (methyl-substituted)	method	"H"	"Me"	$\Delta\Delta E_w$	$\Delta\Delta G_w^{sol}$ [b]	$\delta G^{sol} - \Delta\Delta G_w^{sol}$
1(H) → **1**(+)**b**·H_2**O[*C*$_s$]**	**2**(H) → **2**(+)**b**·H_2**O[*C*$_s$]**	MP2(full)/6- 31G*	−22.4	−19.3	3.1	2.6	−3.8 [−4.1]
		B3LYP/6-311 G**	−22.4	−17.2	5.2	4.4	−0.9 [−1.2]
11(H) → **11**(+)**b**·H_2**O(a)**	**12**(H) → **12**(+)**b**·H_2**O(a)**	B3LYP/6-31 G*	−22.6	−20.4	2.2	1.8	5.0

[a] Using MP2(full)/6-31G*-computed $E(H_2O) = -76.199\,24$ hartrees, B3LYP/6-311G**-computed $E(H_2O) = -76.447\,45$ hartrees, and B3LYP/6-31G*-computed $E(H_2O) = -76.408\,95$ hartrees. [b] Calculated from $\Delta\Delta G^{sol}$ (see Tables 4 and 5 and text).

decrease of the methyl effect due to relative stabilization of the parent bridgehead cations. The accordance between the computed $\Delta\Delta G^{sol}$[R(+)−R(H)] and experimental $\Delta\Delta G^{sol}$[R(+)−R(H)]$_{exp}$ values is surprisingly good. Thus, the differences between computed and experimental hydride affinities of the studied cations, which are listed in Table 3 (δG^{sol}), are comprised within ±1 kcal/mol. The only exceptions are the δG^{sol} values corresponding to solvolytic reactions giving place to rearranged products. In these cases the δG^{sol} are in the range −5.3 to −6.8 kcal/mol.

Solvent effects on the solvolysis rates of bridgehead derivatives have been experimentally studied in the systems **1**,[11] **3**,[3] **7**,[36] **9**,[7] and **11**.[8] Unfortunately, the solvent effect on the methyl effect in the case of the rearranging systems **1**/**2** and **11**/**12** has not been measured experimentally. It has been concluded that strong hydrogen bonding acceptors such as ethanol cause small rate enhancements due to stabilization of the corresponding cations by hydrogen bonding of the bridgehead hydrogens. This type of cation stabilization is not taken into account by the continuum models of the SCRF theory.[34] Consequently, slightly more negative δG^{sol} values result for **3** and **9** in the case of the nucleophilic solvent 80% ethanol in relation to the nonnucleophilic solvents TFE and acetic acid, respectively, due to preferential solvation of the parent cations by hydrogen bonding (Table 3).

Methyl Effect in Solution in the Case of Rearranging Cations. Two mechanisms have been proposed[12] for the rapid solvolysis of bicyclo[1.1.1]pent-1-yl halides: (a) a process involving a **1**(+)[C_s']-like cation as the primary intermediate, (i.e. a reaction in which ionization and ring fragmentation are concerted)[22] and (b) a simple ionization involving a **1**(+)[C_{3v}] cation, rapidly rearranging to a **1**(+)[C_s'']-like cation.[12]

The high solvolysis rates of the bicyclo[3.1.1]hept-1-yl bromides **11**(Br) and **12**(Br) have been attributed to stabilization of the transition state by through-space interactions (vide supra).[8] On the other side, the enhanced solvolysis rates of the parent compounds, **1**(Cl) or **1**(Br), and **11**(Br) in the case of nucleophilic solvents[8,12] has been ascribed to stabilization of the unrearranged transition states by hydrogen bonding.

The accordance between the computed and experimental values in solution (as expressed by the δG^{sol} values) is very good in the case of the unrearranged cations **1**(+)[C_{3v}] and **2**(+)-[C_{3v}]. By contrast, the calculated δG^{sol} values for the rearranged **1**(+)[C_s**]** and **2**(+)[C_s**]** cations as well as for **11**(+) and **12**(+) are very high. Another problem arises from the fact that, according to the PCM model, the solvent effect is only dependent on the dielectric constant (ϵ) but not on specific interactions such as hydrogen bonding and nucleophilic ability.[33,34] Hence, the solvolysis rates of **1**(Br) and **11**(Br) in trifluoroethanol should be very similar to those measured in ethanol, because ϵ values are nearly the same (27.1 vs 24.5), which stands in contrast with the experimental results[8,12]

To clarify this situation, it is interesting to know how the cations interact with an aqueous environment to give the rearranged reaction products. With this purpose, we have optimized the structures of the complexes of cations **1**(+)[C_{3v}], **2**(+)[C_{3v}], **11**(+), and **12**(+) and one water molecule at the MP2(full) and B3LYP theoretical levels using the 6-31G* and 6-311G** standard basis sets. We consider that these methods reproduce cation−water complexation energies satisfactorily.[31]

The directions for the nucleophilic attack of water on cations **1**(+)[C_{3v}] and **2**(+)[C_{3v}] studied are given in Figure 6. Attacks I−III and V lead finally to the rearranged complexes **1**(+)**b**·H_2O[C_s] or **2**(+)**b**·H_2O[C_s] (Table 4). Only frontal attack IV affords complexes with structural retention and nearly C_{3v} symmetry. The corresponding differences in total energies computed with the MP2(full)/6-31G* and B3LYP-31G** methods are listed in Table 4. Zero-point vibrational energy (ZPVE) corrections have not been taken into account due to the flatness of the potential energy surfaces of the water complexes.[31]

The directions followed for the water attack on cations **11**(+)- and **12**(+) are shown in Table 5. The relative total energies (ΔE) of the complexes obtained by optimization with the B3LYP/6-31G* method are listed in Table 5. In the case of attack III on cation **11**(+), two different stationary complexes are formed. At first, complex **11**(+)**b**·H_2O(pe) with boot conformation and pseudoequatorial disposition of the water and, afterward, the chair complex **11**(+)**b**·H_2O(a). The product **11**(OH)**b**(a) (Table 7) results from deprotonation of complex **11**(+)**b**·H_2O(a). The more stable equatorial isomer **11**(+)(**e**) is formed by equilibration of either the axial conformer or between the corresponding precursor water complexes.

The attack of water on cation **12**(+) following direction III affords only complex **12**(+)**b**·H_2O(a), whose deprotonation yields the product **12**(OH)**b**(a). In this case, the kinetically favored conformer is also the (slightly) more stable one. The relative total energies of the products resulting from deprotonation of the complexes and optimization of the resulting alcohols with the B3LYP/6-31G* method are given in Table 7.

If E[R(+)·H_2O] denotes the total energy of the optimized structure of a cation−water complex, E[R(+)] the energy of the cation with the relaxed structure in the complex, and $E(H_2O)$

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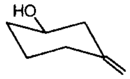
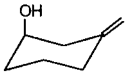
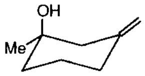
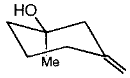
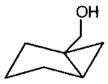
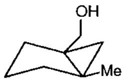
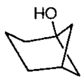
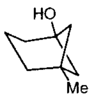
(36) For alkyl substituted adamantanes, see: Takeuchi, K.; Okazaki, T.; Kitagawa, T.; Ushino, T.; Ueda, K.; Endo, T.; Notario, R. *J. Org. Chem.* **2001**, *66*, 2034.

Table 7. B3LYP/6-31G*-Computed Relative Total Energies (ΔE, kcal/mol) of Reaction Products from Nucleophilic Attack of Water on the Corresponding Computed Intermediates **11**(+)·H_2O and **12**(+)·H_2O

Attack	Cation	Complex	Product	ΔE
III	11(+)	11(+)b·H_2O(pe)	 **11(OH)b(e)** ⇌	0.00
	11(+)	11(+)b·H_2O(a)	 **11(OH)b(a)**	1.03
			 **12(OH)b(a)** ⇌	0.01
	12(+)	12(+)b·H_2O(a)	 **12(OH)b(e)**	0.00
II	11(+)	11(+)a·H_2O	 **11(OH)a**	7.40
	12(+)	12(+)a·H_2O(pe)	 **12(OH)a**	13.10
I	11(+)	11(+)·H_2O	 **11(OH)**	9.00
	12(+)	11(+)·H_2O	 **12(OH)**	8.40

the energy of water, then the interaction energy (ΔE_w) between the cation and the water molecule is

$$\Delta E_w = E[R(+)\cdot H_2O] - E[R(+)] - E(H_2O) \qquad (4)$$

The calculated interaction energies (ΔE_w) are listed in Table 6. These values are not corrected for basis set superposition error (BSSE)[37] because we are only interested in relative values. An estimation of the BSSE using the counterpoise method gives BSSEs in the range of 1−3 kcal/mol for weakly bound species, even in the case of basis sets without diffuse functions at the MP2(full) and B3LYP theoretical levels.[31,38,39] From the interaction energies listed in Table 6 can be concluded that the nucleophilic assistance of only one water molecule causes a considerable stabilization ($\Delta\Delta E_w$) of the parent cations in relation to the methyl-substituted cations.

Corrected $\Delta\Delta G^{sol}$ values for the nucleophilic assistance of the solvent (water), given as $\Delta\Delta G_w{}^{sol}$ in Table 6, have been calculated on the following assumptions: (a) only 85% of the total nucleophilic assistance, $\Delta\Delta E$, is manifested in the transition state of the solvolysis; (b) also in solution stands that $\Delta\Delta E \approx \Delta\Delta G$. After correction, a discrepancy of 3.8−0.9 kcal/mol remains between computed (fully corrected) and experimental $\Delta\Delta G^{sol}$ values (Table 6, $\delta G^{sol} - \Delta\Delta G_w{}^{sol}$).

The differential nucleophilic assistance in the case of **11**(+)/**12**(+) was calculated from the ΔE_w value corresponding to the **11**(+)**b**·H_2O(a) and **12**(+)**b**·H_2O(a) complexes, because they represent "product-like" transition states (vide infra), in which the nucleophilic assistance is fully manifested. However, the deviation calculated for this system is very high (Table 6). Seemingly, the differential assistance of only one water molecule is insufficient to account for the higher solvolysis rate of **11**(Br) in relation to **12**(Br).

Therefore, we can conclude that the most probable mechanism for the solvolysis of compounds **1**(Br), **2**(Br), **11**(Br), and **12**(Br) is the ionization concerted with rearrangement (σ-assistance) favored by the nucleophilic attack of the solvent. It is to be expected that the k_{Me}/k_H ratios of the corresponding substrates in the case of nonnucleophilic solvents should be similar to that computed with the PCM model and, hence, higher than the measured in aqueous solvents. Unfortunately, the corresponding k_{Me}/k_H ratios have not been measured in trifluoroethanol in the case of rearranging substrates.

Predicting the Reaction Products. The solvolysis of the halides **1** and **2** in 80% aqueous ethanol affords only 3-methylenecyclobutyl products.[12,22,40] In a reported trapping experiment with azide ion, part of the reaction products (5%) was bicyclo[1.1.0]but-1-ylcarbinyl azide [**1**(N_3)**a**].[22b] Products with structural retention were not isolated in any case.[41] We will now try to discuss the origin of the possible solvolysis products. The water complexes can be considered as transition state (TS) models for the formation of the reaction products. Therefore, considering the relative energies (ΔE) listed in Table 4, the only solvolytic products should be the rearranged alcohols **1**(OH)**b** or **2**(OH)**b** (Figure 6), which is in agreement with the experi-

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(37) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(38) Jansen, H. B.; Ros, P. *Chem. Phys. Lett.* **1969**, *3*, 140.
(39) Han, W.-G.; Suhai, S. *J. Phys. Chem.* **1996**, *100*, 3942.
(40) Maillard, B.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1983**, 900.
(41) However, the related 3-iodobicyclo[1.1.1]pent-1-yl cation can be trapped under special reaction conditions: Milne, I. R.; Taylor, D. K. *J. Org. Chem.* **1998**, *63*, 3769.

Table 8. Relative Energies (ΔE, kcal/mol) of Reaction Products and Corresponding Water Complex Intermediates for the Solvolysis of **11**(Br) at 70 °C

product	ΔE (reacn prod)[a]	ΔE(water complex)[b]	product ratios calc[c]	product ratios expt[d]
11(OH)	9.00	0.00	1.00	1.0
11(OH)a	7.40	1.84	0.10	0.6
11(OH)**b**(e)	0.00	0.73	0.34	1.3

[a] Calculated from the computed ΔE values given in Table 7. [b] Calculated from the ΔE values of Table 5. [c] Calculated from the equation $k_r = -RT \ln \Delta G$, supposing $\Delta G = \Delta E$. [d] From obtained experimental results reported in ref 8b.

mental results (vide supra). The C_{3v} complexes are high-energy species (Table 4) despite the fact that they are favored by the entropy of symmetry $\Delta S = RT \ln(\sigma_{3v} - \sigma_s) = 0.5$ kcal/mol (at 70 °C) against each of the two C_s complexes.

In an attempt to explain the formation of the bicyclic azide **1**(N_3)**a**, a concerted attack of the azide anion following direction III to yield cation **1**(+)[C_{3v}] (Figure 6) have been proposed.[4b] However, we have found that such an attack should afford products of type **1b**. Hence, the azide **1**(N_3)**a** is probably formed by "leakage" to the **1**(+)**a**·N_3[C_s] complex from the more stable azide complex **1**(+)**b**·N_3[C_s], as shown in Figure 6 for the water reaction (see Figure 6, N_3 instead of H_2O).

The products resulting from the solvolysis of **12**(Br) were not determined.[8] The product ratios in the case of **11**(Br)[8] in buffered 80% ethanol at 70 °C are given in Table 8. The corresponding relative total energies (ΔE) computed by us with the B3LYP/6-31G* method are listed in Table 8. There is clearly no relationship between energies and ratios of the reaction products. Thus, the solvolysis is kinetically controlled, just like other reactions in buffered solvents.

The exploration of the potential energy surface of the water complexes of cation **11**(+) resulting from attack III, reveals the existence of two stationary states, **11**(+)**b**·H_2O(a) and **11**(+)-**b**·H_2O(pe) (Table 5). The first one is "product-like" and is relevant for the calculation of the nucleophilic assistance (vide supra). However, the product-determining reaction step for the formation of **11**(OH)**b**(a) is better represented by the "reactant-like" complex **11**(+)**b**·H_2O(pe).

The ΔE values of the water complexes conducting to the products **11**(OH), **11**(OH)**a**, and **11**(OH)**b** are shown in Table 8. Supposing $\Delta E = \Delta G$, the product ratios were calculated using the Boltzmann distribution equation. The accordance between computed and experimental product ratios is surprisingly good, taking into account that the described procedure is the first computational approach to the prediction of product ratios in the solvolysis of rearranging substrates.

Conclusions

The introduction of a bridgehead methyl group always causes the stabilization of the bridgehead carbocations in gas phase in relation to the unsubstituted carbocations. This methyl effect is, however, not manifested in the relative solvolysis rates of bridgehead derivatives in solution due to the relative stabilization of the parent cations according to the PCM model of the continuum solvent theory. In the case of rearranging cations, the differential nucleophilic assistance of solvent is an important contributor to the higher solvolysis rates of the unsubstituted cations. This component of global methyl effect can be satisfactorily accounted for by using simple solvation models. The product ratios in the case of rearranging substrates can be estimated from the relative stability of the intermediate water complexes.

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Supporting Information Available: All optimized structures (GJF) as well as the PCM computations (OUT files) and tables with absolute energies, geometries, and charges of all structures (CIF). This material is available free of charge via the Internet at http://acs.pubs.org.

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