An Experimental and Computational Study about the Effect of a Spirocyclopropane Group on the Solvolysis Rates of Bridgehead Triflates[||]

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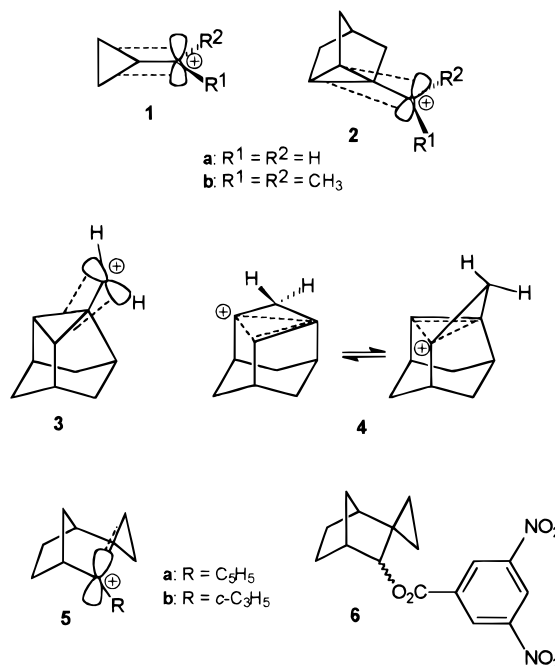
7′,7′-Dimethylspiro[cyclopropane-1,2′-norbornan]-1′-yl triflate (**9**) was obtained and its solvolysis rates in buffered 60% aqueous ethanol were determined at different temperatures. The solvolytic behavior of **9** and other bridgehead derivatives (**13**−**17**, see Table 1) was studied by force-field, semiempirical and ab initio [B3LYP/6-31g(d)] methods. Cation **9**(+) is a slightly pyramidal cyclopropylcarbinyl cation in a nearly perpendicular conformation, showing an sp²-like hybridization. Its high electron demand provokes an enhancement of the σ-participation of the C_5-C_6 and C_4-C_7 bonds. The introduction of a cyclopropyl group adjacent to the bridgehead cation leads to an increase of the strain energy. This fact has two opposite effects on the solvolysis rate: (a) the strain energy hinders the flattening of the cation and, hence, originates a rate depression, and (b) the strained C−C bonds are prone to stabilize the cation at C_1 by σ-delocalization, which provokes a rise of the solvolysis rate. Both effects are accounted for only by the B3LYP/6-31g method. The claimed electron-withdrawal effect of the cyclopropyl group as a basis for the small $k(\mathbf{17})/k(\mathbf{16})$ rate ratio is not confirmed by our calculations.

Introduction

Cyclopropylcarbinyl Cations. The fascinating behavior of cyclopropylcarbinyl derivatives in solvolytic processes has attracted the attention of many chemists over the last 40 years.[1] The most important questions concern the relationship between geometry and solvolysis rate.

The structures of the bicyclobutonium or cyclopropylcarbinyl cations (merely the name was a subject of controversy)[1] generated from cyclopropylmethyl or cyclobutyl derivatives, are among the conceptually most difficult nonclassical carbocations.[2]

The parent cyclopropylcarbinyl cation **1a** (Figure 1) is not static nor the sole species in stable solution (magic acid). The bisected structure **1a** was suggested as a possibility for the minor cation of the species.[3] In the case of dimethylcyclopropylcarbinyl cation **1b** the NMR spec-

Figure 1. Structural diversity of cyclopropylmethyl cations.

tra are consistent with the bisected structure, due to the stabilizing effect of the methyl groups;[4] however, the rotation barrier about the $C_1-C_{1'}$ bond is small (13.2 kcal/mol),[4] so that **1b** cannot be regarded as a static structure. In contrast with **1**, the nortricyclylcarbinyl cations **2** had allowed the first unequivocal observation of the NMR properties of a static (the $C_1-C_{1'}$ barrier to rotation of

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|| This work is dedicated to the late Prof. de Pascual Teresa.

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2b is higher than 18 kcal/mol) and bisected cyclopropylcarbinyl structure.[5] However, the NMR spectra of the very similar triaxane-2-methyl cation **3** are in accord with a static bisected cation (point group C_3) as well as with a rapidly equilibrating mixture of less symmetric cations **4** (bicyclobutonium ions).[6] Both the experimental and computed chemical shifts [IGLO//B3LYP/6-31g(d)] are in good agreement with a fast equilibrium between the structures **4**. The structures of spiro[cyclopropane-3′-norbornan]-2′-yl cations **5** are also bicyclobutonium-like, according to NMR data and low-level (STO-3G) calculations.[7]

The interaction between the electron-deficient carbinyl carbon and the adjacent cyclopropyl group gives rise to a highly geometry dependent stabilization.[1–8] The solvolytic participation of cyclopropyl groups with cationic centers has been investigated for several orientations of the cyclopropyl group in relation to the cationic center.

The rates of solvolysis in 70% acetone–water of *exo*- and *endo*-spiro[cyclopropane-1,3′-norbornan]-2′-yl 3,5-dinitrobenzoates **6** (Figure 1) are strikingly similar, showing little of the large *exo/endo* rate ratio associated with the 2-norbornyl system.[9] Also interesting is the ca. 10^3 rate enhancement of *exo*-**6** over *exo*-2-norbornyl 3,5-dinitrobenzoates. Both experimental data are consistent with the participation of the cyclopropyl group leading to the formation of the highly stabilized cyclobutonium-like cation **5** (R = H) as intermediate (here, only the *exo* lobe of the empty p-orbital interacts with the *exo*-C–C bond of the cyclopropyl group). The only product isolated from the solvolysis was the *exo* alcohol derived from **6**. Accelerations were also observed in the case of geometrically unrestricted cyclopropylcarbinyl derivatives, whose solvolysis takes place through type-**1** cations, affording usually a mixture of rearranged products.[1]

In contrast with this, the solvolysis of spiro[cyclopropane-1,2′-adamantan]-1′-yl chloride [**17(Cl)**] (Table 1) in 50% (v/v) aqueous ethanol at 25 °C takes place slower, by a factor of 1.6×10^{-3}, than the unsubstituted 1-adamantyl chloride **16(Cl)** (Table 1).[10,11] The rate decrease in the case of **17(Cl)** was attributed to the electron-withdrawing effect (−I effect) of the cyclopropyl group adjacent to the bridgehead position where ionization takes place.[10,11] Hence, there is no resonance stabilization of the static perpendicular conformation[1] shown by the intermediate cyclopropylcarbinyl cation **17(+)**.

Bridgehead Cations. There is continued interest in the chemistry of bridgehead cations such as 1-norbornyl

cation **14(+)**[12] (Table 1). The sluggish behavior of 1-norbornyl derivatives toward ionization[13] is the result of their reluctance to accommodate the developing positive charge at the nonplanar bridgehead position.[14] Thus, only the 2-norbornyl cation is observed by NMR upon ionization of 1-chloronorbornane in an SbF_5/SO_2 system at low temperatures.[15] In contrast with this, the 1-adamantyl cation **16(+)** (see Table 1) is readily prepared in solution.[15b,16] The cation **16(+)** is stabilized by carbon–carbon hyperconjugation (σ-participation).[17] The carbon–hydrogen hyperconjugation is not favorable in this system because it would violate Bredt's rule.[15b] Cation **14(+)**, more strained due to its rigid framework, cannot form a planar sp^2 cationic center and will therefore remain relatively unrehybridized, with an empty sp^3-like orbital, which cannot be adequately stabilized by homoconjugation[15b] (according to our calculations this conclusion is not correct; see later).

To carry out a study of structure–reactivity relationships in 1-norbornyl cations, it is convenient to have a series of norbornyl derivatives at ones disposal.[15b,18] We have previously shown that the rearrangement of 2-norbornanones by reaction with triflic anhydride (Tf_2O) is a very useful method for the introduction of the versatile triflate group at the bridgehead position of the norbornane system.[19] In the present work we report about a carbocation system that incorporates features of both the 1-norbornyl cation and a distorted cyclopropylcarbinyl structure, the cation **9(+)**, formed by solvolysis of spiro[cyclopropane-1,2′-norbornan]-1′-yl triflate (**9**) (see Table 1).

Results and Discussion

7,7-Dimethyl-2-methylenenorborn-1-yl triflate (**8**) was obtained by reaction of 1,3,3-trimethyl-2-norbornanone (**7**) with Tf_2O, according to our procedure for the preparation of 1-norbornyl triflates (Scheme 1).[19,20] The synthesis of triflate **9** was achieved by cyclopropanation[21] of the carbinol **10**,[22] due to failure of the reaction between **8** and

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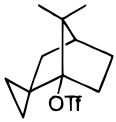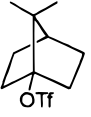
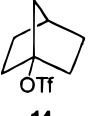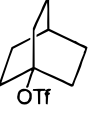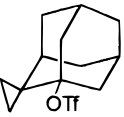(8) Buckley, N. *J. Org. Chem.* **1997**, *62*, 2205.

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Table 1. Rate Constants (k) and Activation Parameters for the Solvolysis of Bridgehead Triflates in Buffered 60% (w/w) Aqueous Ethanol[a]

Substrate	T (°C)	k (s^{-1})[b]	$\Delta H^{\ddagger}$ (kcal·mol^{-1})	$\Delta S^{\ddagger}$ (eu)	Ref.
9	64.5	1.08×10^{-6}	33.9	14	
	73.7	4.47×10^{-6}			
	80.3	1.06×10^{-5}			
13	80.3	1.59×10^{-5}	28.9	-0.8	20
14	80.3	1.08×10^{-5}	26.8	-2.5	20
15	80.3	0.13×10^{2} [c]			
16	80.3	1.19×10^{5} [c]			
17	80.3	0.61×10^{3} [c]			

[a] Solvolysis reactions were performed in closed ampules placed in a thermostat-controlled oil bath. Typical concentrations are [3] = 2.5 × 10^{-2} M, [Et$_3$N] = 5.0 × 10^{-2} M. Decalone was used as internal standard for GLC analysis. [b] Experimental error ±5%. [c] Extrapolated values.[10,11,23]

diiodomethane. The reaction of **11** with Tf$_2$O under the usual reaction conditions[19] afforded a mixture of products. Therefore, new reaction conditions were probed. The best results were obtained by reaction of **11** with methyllithium followed by addition of Tf$_2$O at 0 °C.

The solvolysis of **9** in 60% (w/w) aqueous ethanol with triethylamine as buffer affords only the corresponding bridgehead alcohol **11** and ether **12** in an **11**/**12** = 9/1 ratio, according to GLC analysis. The structure of ether **12** was established unequivocally by comparison with a sample prepared by us from alcohol **11** (Scheme 1). The k values at different temperatures were determined by

GLC. These values as well as the calculated activation parameters are given in Table 1.
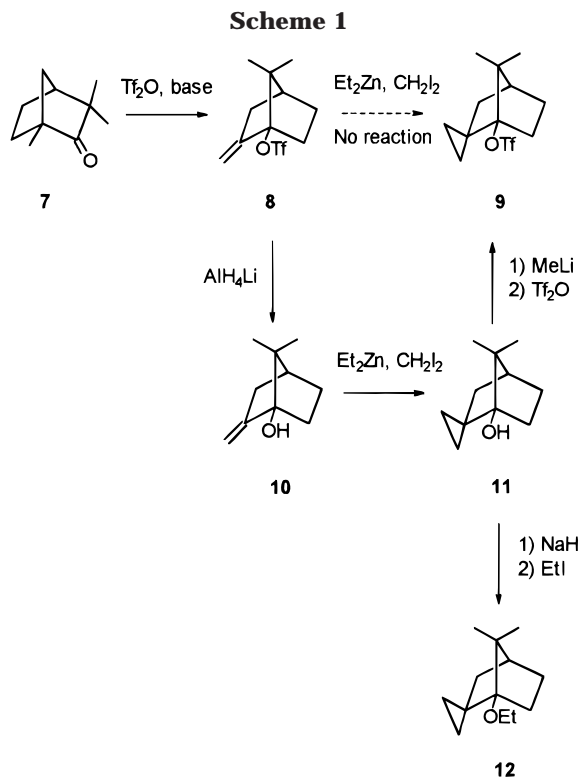
Bicyclo[2.2.2]octan-1-yl triflate (**15**) (see Table 1) shows a strain energy lying between those of **14** and **16** and was included in Table 1 as a reference substrate. The solvolysis rates (k) of the triflates **15–17** in 60% (w/w) aqueous ethanol at 80.3 °C were calculated by us using conversion factors.[23] As shown in Table 1, the solvolysis rate of triflate **17** is 5.2 × 10^{-3} times slower than the rate of triflate **16**. Surprisingly, the solvolysis of the triflate **9** takes place slower than the solvolysis of 7,7-dimethyl-1-norbornyl triflate (**13**)[20] only by a factor of 0.67.

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Scheme 1

Tf₂O, base → Et₂Zn, CH₂I₂ ——————→ No reaction

7 **8** **9**

AlH₄Li

1) MeLi
2) Tf₂O

Et₂Zn, CH₂I₂ →

10 **11**

1) NaH
2) EtI

12

Three possible explanations for the astonishingly high k values of **9** were considered: (a) relief of F-strain[24] due to steric congestion in the ground state of **9**, (b) edge-bridging of the cyclopropyl group leading to a (distorted) bicyclobutonium cation,[1d] and (c) the increasing electron demand[25] generated by the destabilizing effect[10,11,26] of the (nearly) perpendicular cyclopropyl group, which enhances the participation of the σ-bonds of the norbornane framework.

The solvolysis of 1-norbornyl triflate (**14**) in buffered (Et₃N) 60% (w/w) aqueous ethanol takes place with C—O fission and with formation of the 1-norbornyl cation [**14-(+)**] as intermediate.[27] The competition of a S—O bond-cleavage mechanism in aqueous ethanol can be excluded even in the case of the much less reactive 4-nortricyclyl triflate.[27] We have shown[20,27c] that the solvolysis of substituted 1-norbornyl triflates in the same solvent mixture yields a nearly constants ratio (1.50) of bridgehead alcohols (ca. 60%) and ethers (ca. 40%). This ratio is similar to the one found (1.18) in the case of the solvolysis in 70% (v/v) aqueous ethanol of 1-adamantyl

bromide **16(Br)**. Thus, the reaction of bridgehead cations with nucleophiles fulfills the constant selectivity principle.[29] Therefore, the high selectivity (**11/12** = 9.0) showed by the cation **9(+)** is surprising. A possible explanation is the steric hindered attack of ethanol in relation to water, suggesting a steric acceleration for the reverse process (ionization of **9**). Hence, F-strain could contribute to the high k value of **9**.

F-Strain Problem. We decided then to examine the F-strain problem in the solvolysis of bridgehead derivatives.[12c] The existing F-strain is detected by deviations of the straight lines obtained by plotting the logarithm of the rates of solvolysis of bridgehead derivatives vs the changes in steric energies (ΔE_{st}) between the parent bridgehead hydrocarbon (RH) and the corresponding cation (R⁺), calculated by force-field methods.[12c] It was found that, with only a few exceptions,[12c,30] the solvolysis of bridgehead tosylates and triflates is insensitive to F-strain.[12c] To test if F-strain was present in **9**, we have calculated the ΔE_{st} (see Table 2) corresponding to substrates **9(H)** and **13(H)−17(H)** by the MM+ molecular mechanic method implemented in the HyperChem package[31] and plotted[32] $-\ln k$ vs ΔE_{st} (see Figure 2; correlation coefficient $r = 0.987$ excluding **17**). The obtained result was fully unexpected: the F-strain effect was negligible in the case of **9** but high for **17**, the substrate used for the experimental determination of the stability of a cyclopropylcarbinyl cation in perpendicular conformation! (See above.) An F-strain-free rate constant $k(\mathbf{17})_{cal} = 0.13$ s⁻¹ was calculated by linear regression analysis from the deviation of **17**. Thus, the "correct" rate ratio $k(\mathbf{17})_{cal}/k(\mathbf{16})$ should be 1.58×10^{-6} instead of 5.5×10^{-3}. To clarify this unexpected force-field result, it seems convenient to take into account the electronic effects of the framework carbons, which are excluded from the force fields.[33]

Semiempirical Calculations. The semiempirical molecular-orbital method MINDO/3 has been used to give an account of electronic factors in strained bridgehead carbocations.[34] On the other hand, the AM1 method is used for the study of the solvolysis of bridgehead oxonorbornyl triflates.[35] Hence, we have calculated the differences in binding energy (ΔE_b) between the hydrocarbons **9(H)**, **13(H)−17(H)** and the cations **9(+)**, **13(+)−17(+)** by the AM1 and the MINDO/3 methods implemented in HyperChem.[31] The results (ΔE_b^A and ΔE_b^M, respectively) are given in Table 2.

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(33) See, for example: Bentley, T. W.; Roberts, K. *J. Org. Chem.* **1985**, *50*, 5852.

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(35) (a) Takeuchi, K. Yoshida, M.; Ohga, Y.; Tsugeno, A.; Kitagawa, T. *J. Org. Chem.* **1990**, *55*, 6063. (b) Carrrupt, P.; Vogel, P. *J. Org. Chem.* **1990**, *55*, 5696. (c) Martínez, A. G.; Osío, J.; Teso, E. *Tetrahedron* **1996**, *52*, 14041.
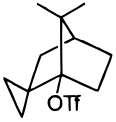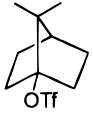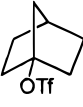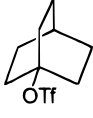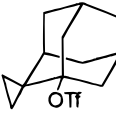
Table 2. Computationally Calculated Energy Differences (kcal/mol) for the Solvolysis of Bridgehead Triflates

Substrate	$-\ln k^a$	$\Delta E_{st}(R^+\text{-}RH)^b$	$\Delta E_b^A(R^+\text{-}RH)^c$	$\Delta E_b^M(R^+\text{-}RH)^d$	$\Delta E(R^+\text{-}RH)^e$
9	11.455	25.26	286.4	225.7	576.3
13	11.049	25.16	287.8	230.2	576.2
14	11.436	23.63	291.6	254.9	583.1
15	-2.565	14.39	271.2	244.9	565.5
16	-11.687	13.97	263.8	249.6	556.8
17	-6.413	15.90	263.4	244.2	558.3

^{a} Values at 80.3 °C. ^{b} Molecular-mechanic MM+ calculation. ^{c} Semiempirical AM1 calculation. ^{d} Semiempirical MINDO/3 calculation. ^{e} Ab initio B3LYP/6-31g(d) calculation.
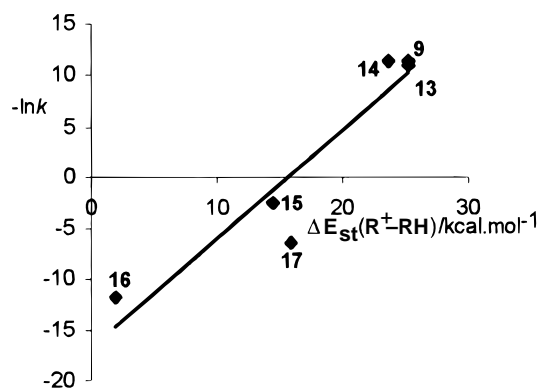

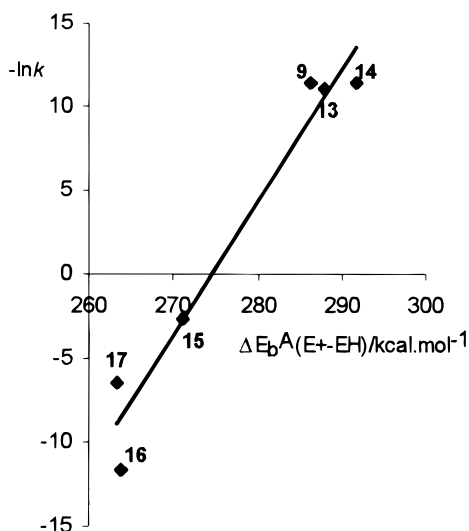**Figure 2.** Lineal correlation of $-\ln k$ vs MM+ calculated ΔE_{st}-$(R^+\text{-}RH)$.

No correlation is observed between ΔE_b^M and $-\ln k$. Moreover, the predicted structures for all cations (available as Supporting Information), with the exception of the 1-norbornyl cation **14**(+), were unrealistically distorted (artifacts), showing the failures of this method to

describe bridgehead cations.[36] In contrast with this, the plot of $-\ln k$ vs ΔE_b^A affords a straight line with a good correlation coefficient ($r = 0.977$) (see Figure 3). As can be seen, according to this method there is no F-strain in the case of **17**. Hence, the deviation of **17** found by the MM+ method must be an artifact.

DFT Calculations. To clarify this contradictory situation as well as to make sure of the bondings in cations **9**(+) and **13**(+)−**17**(+), we sought recourse to the B3LYP method of the density functional theory (DFT).[37] This ab initio method provides significantly greater accuracy than the Hartree−Fock theory with only a small increase in CPU time, because it includes some of the effects of electronic correlation. The choice of the theoretical level is also a matter of novelty, because this method has been scarcely used in the study of structure−reactivity relationships of organic compounds.[38]
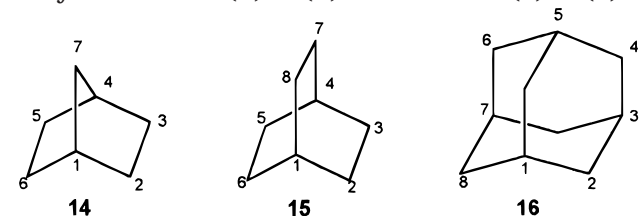
(36) For the deficiencies of MINDO/3, see: Scheleyer, P. v. R.; Sieber, S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1606.
(37) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

Figure 3. Lineal Correlation of $-\ln k$ vs AM1 calculated ΔE_b^A-(R$^+$-RH).

Table 4.   Energies (*E*, in hartrees) of Hydrocarbons 14(H) and 15(H) and Cations 14(+) and 15(+)

	MP2/6-31g(d) (E^M)	B3LYP/6-31g(d) (E^B)	$E^M - E^B$
14(H)	−272.975 91[40]	−273.968 486 4	0.992
14(+)	−272.065 93[40]	−273.040 776 5	0.975
15(H)	−312.147 7[41]	−313.289 914 5	1.142
15(+)	−311.264 2[41]	−312.388 665 2	1.124

GAUSSIAN program package.[39] The structures, energies, and frequencies were calculated at the same theoretical level and basis set [B3LYP/6-31g(d)//B3LYP/6-31g(d)]. Geometries of all stationary points were optimized using self-consistent-field (SFC) and DFT analytical gradient methods. Vibrational frequencies were computed by analytical second-derivative methods.[39] No imaginary frequencies were found.

The bond lengths calculated with the MP2/6-31g(d) method[40,41] are in good agreement with the B3LYP/6-31g-(d) method ($\Delta R = \pm 0.01$ Å; only in the case of $R(2,3)$ of **14(+)** was ΔR 0.03 Å). The concordance with the R values calculated with the AM1 method was bad, because in some cases $\Delta R = 0.05$ Å. There are no high-level studies of the adamantane system (**16**).[17] The R values calculated with the STO-3G method[17] for cation **16(+)** display a slightly better concordance with our B3LYP/6-31g(d) calculation than with the AM1 distances (see Table 3).

Some discussion about the structure of the cations **14-(+)**−**16(+)** is necessary at this point. There is a considerable distortion of the hydrocarbon framework as the cationic center attempts to achieve planarity. There are also some significant changes in bond lengths. The decrease in $R(1,2)$ and increase in $R(2,3)$ in the cations **14(+)**−**16(+)** as well as the decrease in $R(1,7)$ and increase in $R(4,7)$ in **14(+)** indicate substantial hyperconjugation of the cationic center with the β σ(C−C) bonds.[17,40,41,42]

The total energies (i.e., the sum of the electronic energy and nuclear repulsion energy) (E) calculated with ab initio methods for hydrocarbons and cations **14** and **15** are shown in Table 4. The differences between the E values calculated with the MP2 (E^M) and B3LYP (E^B) theoretical levels are given in Table 4. The differences of ca. 1.0 hartrees are due to thermal and/or scaled zero-point energy (ZPE) corrections of the MP2 values.[40,41] We have not attempt to reproduce the MP2 energies by scaling our ZPE values, because we are interested only in the energy differences between cations and hydrocarbons (for the significance of this, see later).
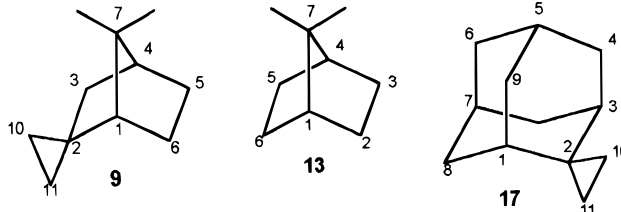
Once the equivalence of the B3LYP/6-31g(d) and MP2/6-31g(d) methods for the study of bridgehead cations has been demonstrated, we have calculated the ΔE(R$^+$-RH) values (see Table 2) corresponding to substrates **9**, **13**, **16**, and **17**, with the same conditions as in the cases of **14** and **15** (see above). Only an imaginary frequency (22i cm^{-1}) was found in the case of **13(+)**, corresponding to a vibration of the C$_4$−C$_5$ (C$_3$−C$_4$) bond (see corresponding structure in Table 5), which was ignored.

The plot of $-\ln k$ vs ΔE(R$^+$-RH) (see Figure 4, solid line) shows clearly that **9** and **13**−**17** are free of F-strain effects, because there are no significant deviations of the correlation line, according with the results of the AM1 method. A slope value near to unity (0.984) for the correlation line points to an essentially complete carboca-

Table 3.   Optimized Bond Lengths (*R*, Å) of Hydrocarbons 14(H)−16(H) and Cations 14(+)−16(+)

14   **15**   **16**

	AM1		MP2/6-31g(d)[40]		B3LYP/6-31g(d)	
R	**14(H)**	**14(+)**	**14(H)**	**14(+)**	**14(H)**	**14(+)**
(1,2)	1.542	1.482	1.538	1.464	1.548	1.470
(2,3)	1.541	1.583	1.557	1.600	1.565	1.567
(3,4)	1.542	1.556	1.538	1.559	1.548	1.611
(4,7)	1.550	1.591	1.536	1.583	1.544	1.593
(7,1)	1.550	1.507	1.536	1.471	1.544	1.480

	AM1		MP2/6-31g(d)[41]		B3LYP/6-31g(d)	
R	**15(H)**	**15(+)**	**15(H)**	**15(+)**	**15(H)**	**15(+)**
(1,2)	1.526	1.471	1.532	1.449	1.542	1.456
(2,3)	1.523	1.569	1.546	1.626	1.559	1.638
(3,4)	1.526	1.539	1.532	1.527	1.542	1.538

	AM1		STO-3G[17]		B3LYP/6-31g(d)	
R	**16(H)**	**16(+)**	**16(H)**	**16(+)**	**16(H)**	**16(+)**
(1,2)	1.526	1.468		1.497	1.544	1.459
(2,3)	1.526	1.574		1.590	1.544	1.628
(3,4)	1.526	1.525		1.540	1.544	1.536

First, we have calculated the structures and energies of the hydrocarbons and cations of the types **14**−**16**, to compare the results with those obtained by using other methods (see Table 3). The calculations were performed with the standard 6-31g(d) basis set implemented in the

(38) (a) Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. R. *J. Org. Chem.* **1997**, *62*, 4216. (b) Smith, B. J.; Tsanaktsidis, J. *J. Org. Chem.* **1997**, *62*, 5709.

(39) Frisch, M. J.; Trucks, G. W.; Schelegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Haman, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foreseman, G. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94W; Gaussian Inc.: Pittsburgh, PA, 1995. Licensed to A. G. Martínez.
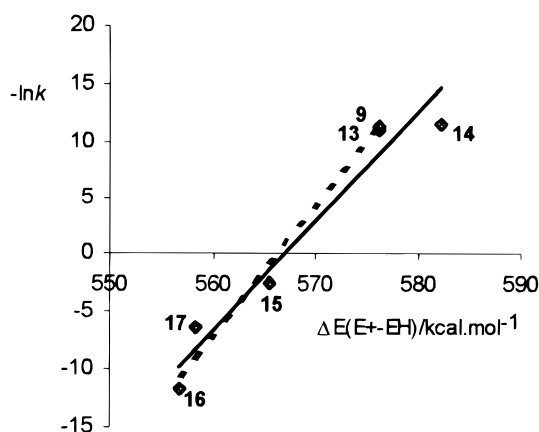
(40) Adcock, W.; Clark, C. I.; Schiesser, C. H. *J. Am. Chem. Soc.* **1996**, *118*, 11541.

(41) Hrovat, D. A.; Borden, W. T. *J. Org. Chem.* **1992**, *57*, 7, 2519.

(42) Grob, C. A.; Rich, R. *Tetrahedron Lett.* **1978**, *29*, 663.

Table 5. Some Significant B3LYP/6-31g(d) Optimized Bond Lengths (Å) for Hydrocarbons 9(H), 13(H), and 17(H) and Cations 9(+), 13(+), and 17(+)

R	9(H)	9(+)	13(H)	13(+)	17(H)	17(+)
(1,2)	1.537	1.484	1.549	1.537	1.531	1.460
(2,3)	1.575	1.559	1.565	1.553	1.531	1.595
(3,4)	1.549	1.556	1.549	1.540	1.545	1.538
(4,5)	1.550	1.588			1.544	1.536
(5,6)	1.565	1.620			1.544	1.534
(1,6)	1.549	1.464				
(1,7)	1.564	1.491	1.563	1.399		
(1,4)	2.251	1.979				
(4,7)	1.565	1.623	1.563	2.199		
(2,10)	1.508	1.521			1.508	1.502
(2,11)	1.507	1.505			1.508	1.502
(10,11)	1.511	1.503			1.514	1.521
(7,8)					1.544	1.633
(1,8)					1.545	1.457
(4,H)	1.095	1.093	1.085	1.090		

Figure 4. Lineal correlation of $-\ln k$ vs B3LYP/6-31g(d) Calculated $\Delta E(R^+\text{-}RH)$.

tionic transition state, in agreement with other experimental results.[23c] The correlation coefficient is good ($r = 0.967$), taking into account the wide range of correlated bridgehead reactivities and the use of extrapolated k values. However, an improved r value of 0.988, i.e., an excellent correlation, could be reached by excluding **14** (see Figure 4, dotted line). This fact suggests that the theoretical level B3LYP with the 6-31g(d) basis set tends to lower the hyperconjugation[38] in the case of **14(+)** by ca. 6 kcal/mol.

At this point, we shall address an interesting question. The well-known Eyring's equation correlates $\ln k$ with free energies (G), not energies (E). However, the structure-reactivity relationships in solvolytic reactions are always discussed by plotting energies or enthalpies against $\ln k$.[12c,40-43] Although a frequency job using

(43) (a) Mareda, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1280. (b) Della, E. W.; Head, N. J.; Janowski, W. K.; Schiesser, C. H. *J. Org. Chem.* **1993**, *58*, 7876. (c) Della, E. W.; Grob, C. A.; Taylor, D. K. *J. Am. Chem. Soc.* **1994**, *116*, 6159. (d) Wiberg, K. B.; McMurdie, N. *J. Am. Chem. Soc.* **1994**, *116*, 11990. (e) Della, E. W.; Janowski, W. K. *J. Org. Chem.* **1995**, *60*, 7756.

GAUSSIAN produces G values, we have also adopted the use of E values taking into account the following considerations. The ZPE and thermal-energy (at 298 K) corrected G value of **13(+)** is $-351.486\ 291$ hartrees. The uncorrected total energy E is $-351.672\ 630\ 4$ hartrees. For **13(H)**, the calculated values are $G = -352.388\ 591$ hartrees and $E = -352.590\ 941\ 2$ hartrees. Thus, $\Delta G(R^+\text{-}RH) = 566.2$ kcal/mol and, hence, $\Delta E - \Delta G = 10.0$ kcal/mol. In the case of the most reactive substrate **16**, a value of $\Delta E - \Delta G = 8.1$ kcal/mol is obtained. Considering the accuracy of the B3LYP/6-31g(d) method (ca. 2 kcal/mol for ΔE),[36] the use of ΔE or ΔG is irrelevant for the calculation of both the slope and the correlation coefficient.
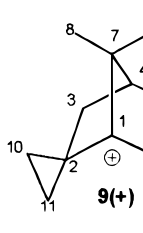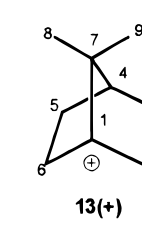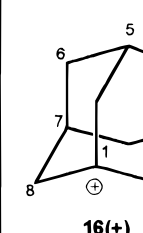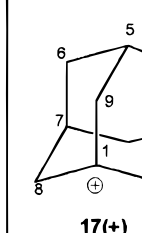
The existing correlation between $\Delta E(R^+\text{-}RH)$ and solvolysis rates provides strong evidence on behalf of that the rate ratios $k(\mathbf{13})/k(\mathbf{9})$ and $k(\mathbf{17})/k(\mathbf{16})$ are mainly due to electronic effects accounted for by the B3LYP/6-31g-(d) method. To determine the nature of these effects, we will take into account the bond lengths (see Table 5) as well as the charge distributions calculated by the Mulliken population analysis (see Table 6). The shorter $R(1,4)$ and $R(1,6)$ distances as well as the longer $R(4,7)$ and $R(5,6)$ distance of **9(+)** when compared with those of the hydrocarbon **9(H)** suggest that the canonical structures **9'(+)** and **9''(+)** (see Figure 5) play an important role in stabilizing cation **9(+)**. Cationic charges (Table 6) also suggest that the resonance structures **9'(+)** and **9''(+)** are important contributors to the overall structure. The C_4–H bond suffers no lengthening in cation **9(+)**, showing that the back-lobe interaction with the empty orbital at C_1 is insufficient to become a stabilizing factor.[40] The slight lengthening of the C_2–C_{10} bond of **9(+)** in relation to the C_2–C_{11} bond probably results from a better overlapping with the empty orbital at C_1 [Figure 6; cf. LUMO (ψ^2) of **17(+)**]. However, the C_2–C_{10} bond lengthening (see Table 5) seems to be too small to cause any significant stabilization of cation **9(+)**. According to our calculations, the empty orbital of **9(+)** looks much like a p-orbital (see Figure 6), strongly suggesting an sp^2-like hybridization for C_1, which is against the proposed sp^3 for the cationic carbon in the analogue cation **14(+)**.[15b] The higher ψ^2 value of the internal lobe for the LUMO of **9(+)** is also pointing to the σ-participation of the norbornane-cage C–C bonds.
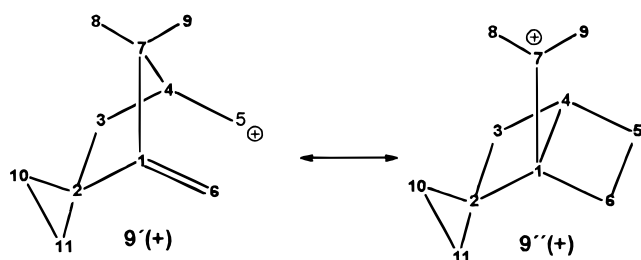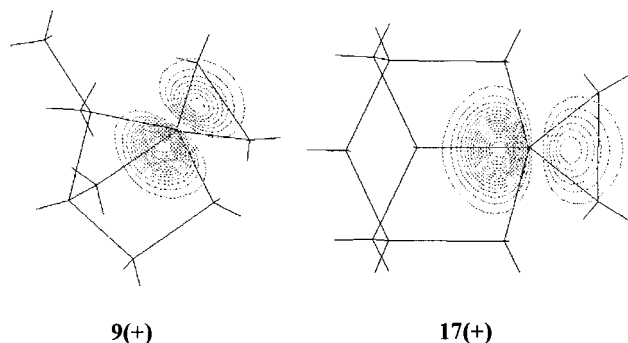
In the case of **13**, the distortions of the above-mentioned bonds in going from **13(H)** to **13(+)** are not so pronounced (see Table 5). Therefore, we believe that the strikingly high solvolysis rate of triflate **9** is mainly due to σ-participation of the C_5–C_6 and C_4–C_7 bonds. Hence, the introduction of the spirocyclopropane group provokes an enhancement of the σ-participation. The same conclusion is reached in the adamantane system by comparing the length variations of the C_1–C_2 and C_2–C_3 bonds provoked by the hydride-abstraction reaction from the hydrocarbons **16(H)** (see Table 3) and **17(H)** (see Table 5). In fact, the rate enhancement in the norbornane system is higher than in adamantane. Thus, the difference in the calculated ΔE values for **9** and **13** is 0.1 kcal/mol, but 1.5 kcal/mol for **16** and **17** (from values given in Table 2). Hence, the strikingly different values of the rate ratios $k(\mathbf{9})/k(\mathbf{13})$ and $k(\mathbf{17})/k(\mathbf{16})$ are accounted for by the DFT method.

On the other hand, the enhancement of σ-participation in cation **9(+)** is accompanied by a loosening of the C–C

Table 6. B3LYP/6-31g(d) Atomic Charges (Hydrogens Summed into Carbons) Calculated on the Optimized Geometry of Cations 9(+), 13(+), 16(+), and 17(+)

C	9(+)	13(+)	16(+)	17(+)
1	+0.175	+0.094	+0.241	+0.190
2	+0.046	+0.138	+0.930	+0.061
3	+0.113	+0.090	+0.063	+0.039
4	+0.049	+0.050	+0.098	+0.095
5	+0.132			+0.060
6	+0.123			+0.094
7	+0.206[a]	+0.400[a]		
10	+0.094			+0.059
11	+0.059			+0.059

[a] Charge sum of C_7, C_8, and C_9.

Figure 5. Canonical structures of cation **9(+)**.

Figure 6. B3LYP/6-31g(d) calculated LUMOs (ψ^2) of cations **9(+)** and **17(+)**.

bond cage in relation to triflate **9**, as well as by a charge dispersion. These two effects can explain the high $\Delta S^{\ddagger}$ value obtained for the solvolysis of triflate **9** (see Table 1).

Therefore, there are two reasons for the enhancement in σ-participation caused by the spirocyclopropane group: (a) the $-I$ effect of the cyclopropyl group (see above) and (b) the increase of strain energy.[44]

Inductive effects, like atomic charges, are not a quantum-mechanical observable (the Mulliken population analysis is only a convention for assigning charges). The theory of atoms in molecules[45] predicts that the cyclopropyl group is somewhat more electron-withdrawing that a methyl (CH_3) group. According with this, the F-value measured for the cyclopropyl group (0.02) is slightly higher than the corresponding one for a methyl group (0.01).[45] Thus, it seems not possible that the $-I$ effect of the cyclopropyl group could provoke the small value of $k(\mathbf{17})/k(\mathbf{16})$. On the other hand, the $-I$ effect of the cyclopropyl group should be detected by higher positive charge at the adjacent carbon C_3. This prediction is correct in the case of **9(+)** [cf. **13(+)**] but fails for **17-(+)** [cf. **16(+)**] (see Table 6). Therefore, the weak $-I$ effect of the cyclopropyl group is overcome by the strong electron-withdrawing ability of the cationic carbon C_1.

(44) The solvolysis of very strained bridgehead derivatives (i.e., cubyl triflate) takes place with enhanced σ-participation: (a) Eaton, P. E.; Yang, C. X.; Xiong, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3255. (b) Hrovat, D. A.; Borden, T. *J. Am. Chem. Soc.* **1990**, *112*, 3227. (c) Wiberg, K. B.; Hadad, C. M.; Sieber, S. Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 5820. (d) Della, E. W.; Head, N. J.; Janowski, W. K.; Schiesser, C. H. *J. Org. Chem.* **1993**, *58*, 7876. (e) Della, E. W.; Grob, C. A.; Taylor, D. K. *J. Am. Chem. Soc.* **1994**, *116*, 6159.

(45) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001.

(46) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

Hence, the increase in strain energy is the main reason for the enhanced σ-participation.

Summary and Conclusions

The relationship between solvolysis rates and strain energies calculated by force-field methods is not a reliable method for the evaluation of F-strain, despite the high correlation coefficient that could be reached.

The semiempirical MINDO/3 method should not be used for calculations on bridgehead cations. The AM1 method is a better one, although some important features are not accounted for by it.

The B3LYP theoretical level with the 6-31g(d) basis set gives a satisfactory explanation of the striking problem of the effect of a spirocyclopropane group on the stability of the corresponding bridgehead cations. However, B3LYP/6-31g(d) fails in describing σ-participation (homoconjugation) in the case of the parent 1-norbornyl cation [**14(+)**] by ca. 6 kcal/mol. The B3LYP/6-31g(d) method calculates cation **9(+)** as a slightly pyramidal cyclopropylcarbinyl cation in a nearly perpendicular conformation, showing an sp^2-like hybridization for the cationic center.

The introduction of a spirocyclopropane group adjacent to the bridgehead position causes an increase of the strain energy, which hinders the flattening of the corresponding cations and, therefore, leads to a solvolysis-rate depression. However, this effect is partially compensated by an enhancement of the σ-participation of the framework $C-C$ bonds, particularly in the case of the very strained norbornane system.

The claimed $-I$ effect of the cyclopropane group as an explanation for the small $k(\mathbf{17})/k(\mathbf{16})$ rate ratio is not confirmed by the DFT method.

Experimental Section

General Information. All starting materials and reagents were obtained from well-known commercial suppliers and were used without further purification. THF and hexane were dried by distillation over sodium/benzophenone under a positive pressure of Ar, and CH_2Cl_2 was distilled from P_2O_5 under a positive pressure of Ar, immediately prior to use. Flash chromatography was performed over silica gel (230−400 mesh). ^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer for ^1H and on a 75 MHz spectrometer for ^{13}C. Chemical shifts (δ) for ^1H and ^{13}C NMR were recorded in ppm downfield relative to the internal standard tetramethylsilane (TMS), and coupling constants (J) are in Hz. IR spectra were recorded in a FT spectrometer. Wavenumbers are in cm^{-1}. Mass spectra were recorded on a 60 eV mass spectrometer. For gas−liquid chromatography, a chromatograph equipped with a capillary OV 101 column was used.

7′,7′-Dimethylspiro[cyclopropane-1,2′-norbornan]-1′-ol (11). Compound **11** was obtained according to the cyclopropanation procedure described by Nishimura, Kawabata, and Furukawa.[7a] Over a solution of hydroxyolefin **10** (1.000 g, 6.58 mmol) in 10 mL of dry hexane, under an Ar atmosphere, were added 11.4 mL of diethylzinc 1 M in hexane (11.40 mmol) followed by dropwise addition via syringe of diiodomethane (4.224 g, 15.76 mmol) over a 30 min period. Exothermic reaction took place immediately. When the addition was complete, the reaction mixture was kept at room temperature for 3 h (the reaction progress was monitored by GLC). Finally, the reaction mixture was poured into 10% HCl, extracted with hexane, washed with water and saturated sodium bicarbonate, and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 60:40) to yield pure **11** (983 mg, 90% yield), as a colorless oil: IR (CCl_4) ν 3610, 3480, 3060 cm^{-1}; MS m/z 166 ($M^{•+}$, 1); ^1H NMR (300 MHz, $CDCl_3$) δ 1.97−1.92 (m, 2H), 1.73−1.65 (m, 4H), 1.41−1.37 (m, 2H), 1.03 (s, 3H), 0.98 (s, 3H), 0.77 (m, 1H), 0.43−0.35 (m, 2H), 0.25 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 82.1, 47.3, 42.2, 39.9, 32.8, 27.8, 26.6, 19.4, 19.1, 13.8, 6.9 ppm.

7′,7′-Dimethylspiro[cyclopropane-1,2′-norbornan]-1′-yl Triflate (9). Over a solution of 300 mg (1.81 mmol) of spiro alcohol **11** in 5 mL of dry CH_2Cl_2, at −78 °C under an Ar atmosphere, were added 1.7 mL of methyllithium 1.6 M in ether (2.72 mmol) followed by dropwise addition of freshly distilled triflic anhydride (0.767 g, 2.72 mmol) via syringe. The reaction mixture was then allowed to warm to room temperature and stirred for 30 min (the reaction progress was monitored by GLC). Finally, the reaction was hydrolyzed with saturated sodium bicarbonate, extracted with CH_2Cl_2, washed with brine, and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by column chromatography (silica gel, hexane) to yield pure **3** (405 mg, 75% yield) as a colorless liquid: IR (CCl_4) ν 3070, 1405, 1210, 1150 cm^{-1}; MS m/z 283 ($M^{•+} - 15$, 2); ^1H NMR (300 MHz, $CDCl_3$) δ 2.43 (m, 1H), 2.27 (m, 1H), 2.14−2.07 (m, 2H), 1.75 (m, 1H), 1.57 (m, 1H), 1.49 (d, $J = 11.7$, 1H), 1.20 (s, 3H), 1.11 (s, 3H), 1.07 (m, 1H), 0.81 (m, 1H), 0.49 (m, 1H), 0.42 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 118.3 (c, $J = 319$), 49.2, 39.9, 39.7, 29.3, 27.8, 26.6, 19.1, 18.8, 14.1, 6.6 ppm.

7′,7′-Dimethylspiro[cyclopropane-1,2′-norbornan]-1′-yl Ethyl Ether (12). Sodium hydride (80 mg, 60% dispersion in mineral oil, 2.00 mmol) was placed in a flask under an Ar atmosphere and washed via syringe, with dry hexane (2 × 3 mL) and with dry THF (1 × 3 mL), to remove the mineral oil. Then, 5 mL of dry THF was added. Over the resultant suspension, 150 mg (0.90 mmol) of spiro alcohol **5** dissolved in 2 mL of dry THF was added dropwise at room temperature. The reaction mixture was stirred for 1 h, and 624 mg (4.00 mmol) of freshly distilled iodoethane was added dropwise via syringe. When the addition was complete, the mixture was refluxed for 6 h (the reaction progress was monitored by GLC). The mixture was poured into saturated ammonium chloride solution, extracted with ether, washed with brine, and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by column chromatography (silica gel, hexane) to yield pure **12** (155 mg, 89% yield) as a colorless liquid: IR (CCl_4) ν 3070 cm^{-1}; MS m/z 194 ($M^{•+}$, 6); ^1H NMR (300 MHz, $CDCl_3$) δ 3.38 (m, 2H), 2.03−1.91 (m, 3H), 1.67−1.27 (m, 4H), 1.05 (s, 3H), 1.04 (t, $J = 6.6$, 3H), 1.01 (m, 1H), 1.00 (s, 3H), 0.40 (m, 1H), 0.28 (m, 1H), 0.15 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 85.2, 60.6, 47.9, 42.2, 40.6, 27.5 (two signals), 27.3, 20.3, 19.4, 16.5, 13.8, 8.0 ppm.

Supporting Information Available: B3LYP Cartesian coordinates corresponding to the optimized geometries of hydrocarbons and cations of types **9** and **13−17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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