Ab Initio Investigations of Perhydrotriquinacenyl and other Bridgehead Carbocations

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Ab initio MO calculations at the SCF level using 6-31G* basis sets show that only 2.1 kcal mol^{-1} more energy is needed to form perhydrotriquinacenyl cation 1 from the corresponding hydrocarbon than to form the tert-butyl cation from 2-methylpropane; such a stabilisation energy is comparable to those computed for 1-noradamantyl cation 2, 3-noradamantyl cation 3, and bicyclo[3.2.1]octan-1-yl cation 4, which are shown to be stabilized efficiently by C–C hyperconjugation.

The lower reactivity of bridgehead derivatives has been attributed to the fact that strain increases dramatically when passing from ground state to transition state, since the intermediate carbocation cannot attain optimal planar geometry owing to skeletal restrictions. In the pioneering work of Schleyer et al.[1] and subsequently in our own work,[2,3] the strain energy accumulated during the formation of the intermediate carbocation has been correlated with the solvolysis rates of bridgehead substrates. This approach uses bridgehead carbocations as a model for transition states of solvolytic processes. Specific force-field parameters have been

developed and incorporated into the molecular mechanics program in order to calculate the strain energy of bridgehead carbocations. This method has been used successfully to correlate the structure and reactivity of numerous tertiary substrates covering a wide range of solvolysis rates.[1–4]

A controversy emerged over perhydrotriquinacenyl derivatives. It had previously been reported that the acetolysis of perhydrotriquinacene toluene-p-sulfonate is 10⁹ times slower than predicted by strain calculations;[1a,b] at that time, this anomaly was rationalized by the unusual instability of perhydrotriquinacenyl cation 1 as being due to the absence of

Table 1 *Ab initio* total and stabilization energies for tertiary cations

| | Cation | Point group | Total energy/au | | $\Delta E_i{}^a$/kcal mol^{-1} 6-31G* |
			3-21G	6-31G*	
1	Perhydrotriquinacenyl	C_3	-385.007401	-387.150708	2.1
2	1-Noradamantyl	C_s	-346.188352	-348.108954	2.9
3	3-Noradamantyl	C_s	-346.179722	-348.101165	7.7
4	Bicyclo[3.2.1]octan-1-yl	C_1	-308.528652	-310.244319	2.4
8	*tert*-Butyl	C_{3h}	—	-156.44241^b	0.0

^{a} Stabilization energy ΔE_i for eqn. (1). ^{b} Ref. 14.

1   **2**   **3**   **4**
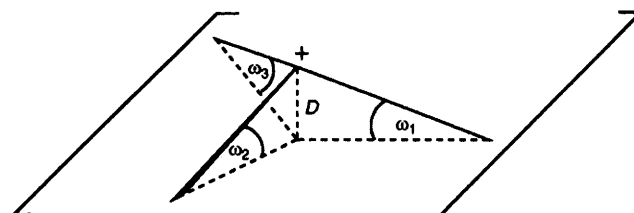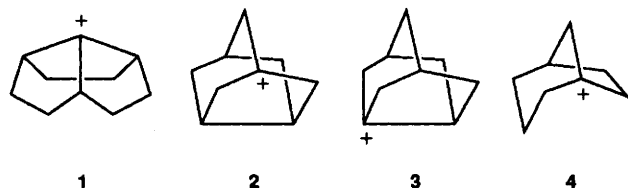
hyperconjugative stabilization, whereas the majority of bridgehead cations do benefit from such stabilizing interactions. In contrast to this finding, our recent MM2-based structure–reactivity relationship study concludes that there should be no abnormal solvolysis rate for perhydrotriquinacenyl derivatives.[3,4a] Nevertheless, in its present stage of sophistication, the MM2 method is not specifically adapted to deal with phenomena such as the hyperconjugation or partial bridging of carbocations. It has therefore become of interest to investigate these properties for a series of bridgehead carbocations with *ab initio* MO theory at the SCF level, using the basis set with polarized functions. In this communication, we report the results of *ab initio* calculations for perhydrotriquinacenyl cation **1**. Its stabilization energy is compared with those of two cage-type ions, 1-noradamantyl and 3-noradamantyl cations **2** and **3**, and with that of the more flexible bicyclo[3.2.1]octan-1-yl cation **4**.

Ab initio MO calculations were carried out using the GAUSSIAN-90 series of programs,[5] on the Cray-2 computer of the Ecole Polytechnique in Lausanne. The CHEM-X program[6] was used for pre- and post-processing of *ab initio* computations. The geometries of all stationary points were fully optimized with analytical gradient methods at Hartree–Fock level using the 3-21G and 6-31G* basis sets. Unless otherwise stated, total and relative energies quoted in the text, as well as geometry parameters, correspond to 6-31G* optimized values.

An extensive *ab initio* investigation of the potential energy surface of perhydrotriquinacenyl cation **1**, followed by vibrational frequencies analysis at the 6-31G*//6-31G* level, revealed that the lowest minimum for this ion has C_3 symmetry. This contrasts with previously reported semiempirical calculations,[7] where the C_{3v} isomer of **1** was suggested to be the minimum. The computed total electronic energies for ions **1–4** are listed in Table 1.

Ab initio calculations predict a moderate pyramidalization at the cationic centre of the perhydrotriquinacenyl cation **1** of C_3 symmetry, as evidenced by an average out-of-plane bending angle θ of 9.9° (Fig. 1). This isomer is in fact one of the least pyramidalized ions in the series under investigation (Fig. 2). Its average out-of-plane bending angle θ is comparable to those computed for other bridgehead carbocations such as: 1-adamantyl,[3,8] and bicyclo[2.2.2]octan-1-yl,[3,9] ($\theta = $ 9.3 and 9.7°, respectively). Ion **1**, however, is clearly less pyramidalized than bicyclo[2.2.1]heptan-1-yl cation,[3,10] where θ is 13.7°.

For cation **1**, no carbon–carbon bond is suitably aligned parallel to the vacant p-orbital of the cationic centre, which

Fig. 1 Pyramidalization at the cationic centre is expressed as the average angle, θ, of the out-of-plane bending angles ω_i of the central atom, relative to the plane defined by the three neighbouring carbons

1 (C_3)
$\theta = 9.9°$

2 (C_s)
$\theta = 10.9°$

3 (C_s)
$\theta = 12.6°$
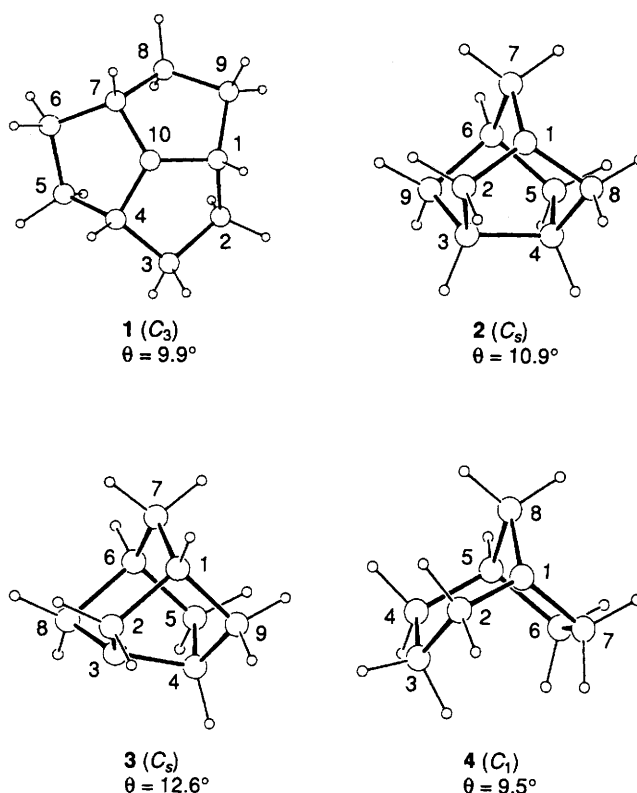
4 (C_1)
$\theta = 9.5°$

Fig. 2 Perspective drawings of the 6-31G* optimized structures of bridgehead carbocations **1–4**; the average out-of-plane bending angle θ (a measure of pyramidalization) is also shown

would allow efficient C–C hyperconjugation. Nevertheless, owing to the pronounced propeller-like arrangement of the three rings in ion **1**, three out of the six α,β C–C bonds have a somewhat improved alignment with the vacant p-orbital of the cationic centre. This results in a weak hyperconjugative interaction, as reflected by the slight lengthening of bonds C(1)–C(2), C(4)–C(5) and C(7)–C(8) to 1.569 Å compared

with 1.545 Å for C(1)–C(9), C(3)–C(4) and C(6)–C(7).† The angle C(10)–C(1)–C(2), and its two symmetry-related angles, are decreased to 98.5°, whereas C(10)–C(1)–C(9) amounts to 102.4°. Such small modifications of geometry have to be interpreted, however, with caution, and this weak three-fold C–C hyperconjugation should be confirmed by geometry optimizations including electron correlation.

In comparison with the cup-shaped ion 1, the geometries of cage-type bridgehead cations are significantly affected by C–C hyperconjugation. In 3-noradamantyl cation 3, two α,β C–C bonds are almost parallel to the vacant p-orbital and their bond lengths are considerably increased. Both distances, C(1)–C(2) and C(6)–C(8), attain 1.606 Å, as compared with 1.540 Å for C(1)–C(9) and C(6)–C(5). The C–C hyperconjugation is also associated with a decreasing C+–C–C bond angle. For cation 3, bond angles of 89.7° were found for C(1)–C(2)–C(3) and C(3)–C(8)–C(6), and these are smaller than that of C(3)–C(4)–C(9) (99.4°). Based on X-ray structure determination, Laube[11] reported a similar lengthening of α,β C–C bond distances (1.62 Å), but a larger C+–C–C angle (99°) for 3,5,7-trimethyl-1-adamantyl cation. Three carbon–carbon bonds are nearly parallel to the vacant p-orbital of carbocations 2 and 4, and the inspection of their optimized structures shows in both cases evidence of several C–C hyperconjugative interactions. Especially noteworthy is the lengthening of the C(2)–C(3) bond to 1.6 Å for cation 4. The partial flexibility of its skeleton permits an ideal parallel orientation of this particular bond to the vacant p-orbital.

The energy of the isodesmic hydride transfer reaction [eqn. (1)] can be calculated using the total electronic energies computed with the ab initio method. In such a hypothetical chemical transformation, the number of bonds of a given formal type is retained, but their relation to one another is altered when passing from reactants to products.[12] The isodesmic energy changes, ΔE_i, listed in the last column of Table 1, are also referred to as tert-butyl cation stabilization energies. For reference, total electronic energies have also been computed for the neutral molecules 5, 6, 7 and 9, and are compiled in Table 2.‡

$$R^+ + CH(CH_3)_3 \rightarrow R–H + C^+(CH_3)_3 \qquad (1)$$
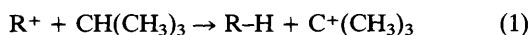
Ab initio calculations predict that more energy is required to generate carbocations 1–4 from their corresponding hydrocarbons than is needed to form tert-butyl cation 8 from 2-methylpropane 9. For ions 2 and 4, ΔE_i is in the range of 2–3 kcal mol⁻¹. Such a small value for ΔE_i reflects the stabilization of these ions by C–C hyperconjugation. Perhy-

drotriquinacenyl cation 1 is one of the most stable in the series under investigation, since its formation from perhydrotriquinacene 5 requires only 2.1 kcal mol⁻¹. When bicyclo-[2.2.1]heptan-1-yl cation was examined in an analogous isodesmic relationship, it was shown to need 15.6 kcal mol⁻¹.[13] This is some 13 kcal mol⁻¹ more than the energy necessary to form perhydrotriquinacenyl cation 1.

The present computations, which relate to the gas phase, show that perhydrotriquinacenyl cation 1 has a stabilization energy comparable to that of other bridgehead carbocations 2–4. Admittedly, the relevance of relative stabilities of cations in the gas phase to solvolytic processes remains open to debate. However, a good correlation between experimental gas phase heterolytic bond dissociation energies and the corresponding rate constants of solvolysis in solution has recently been reported for bridgehead derivatives.[16] In the light of this finding, it is reasonable to use ab initio computed stabilization energies (Table 1) to argue that perhydrotriquinacenyl substrates should display solvolysis rates comparable to those of 1-noradamantyl, 3-noradamantyl and bicyclo[3.2.1]octan-1-yl derivatives.[3,4a]

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Table 2 Ab initio total energies of neutral molecules

Molecule	Point group	Total energy/au	
		3-21G	6-31G*
5 Perhydrotriquinacene	C_3	−385.875740	−388.010691ᵃ
6 Noradamantane	C_{2v}	−347.054705	−348.970068
7 Bicyclo[3.2.1]octane	C_s	−309.393236	−311.104643
9 2-Methylpropane	C_3	—	−157.298978

ᵃ See also ref. 15.

† The discussion of the structures refers to the numbering of atoms in Fig. 2.

‡ Our computed electronic energy for 5 is slightly lower than that reported by Schulman.[15]

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