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# Ab Initio Calculations Find That Formation of Cubyl Cation Requires Less Energy Than Formation of 1-Norbornyl Cation

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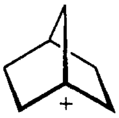
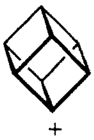
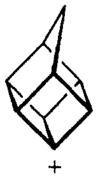
The unreactivity of bridgehead-substituted bicyclo[2.2.1]heptanes toward $S_N1$ solvolysis has been attributed[1] to the increase in strain energy attendant upon forming bridgehead carbocations[2] like $1^+$, in which the constraints of a polycyclic skeleton inhibit the attainment of the planar geometry that is preferred by carbocations. Schleyer and co-workers[3] and, subsequently, Müller and co-workers[4] have found a good correlation between the increase in strain energy, calculated by molecular mechanics, and the negative logarithm of the relative rate of solvolysis for a variety of bridgehead systems. Rates of formation of bridgehead free radicals have also been found to correlate with calculated increases in strain energies.[3b]



$1^+$



$2^+$



$3^+$

On the basis of the highly pyramidalized geometry at the cationic carbon expected in both cubyl ($2^+$) and 4-homocubyl ($3^+$) cations, one would anticipate that the rates of the solvolysis reactions leading to $2^+$ and $3^+$ would be considerably slower than those leading to $1^+$. Indeed, molecular mechanics calculations predict that the triflate precursor of $2^+$ should be unreactive toward solvolysis even at 250 °C.[3b] Nevertheless, Rüchardt and co-workers[5] found that $3^+$ is formed under conditions where the same type of precursor of $1^+$ is totally inert. Moreover, similar results for the rate of formation of $2^+$, relative to that of $1^+$, have been found subsequently by the groups of Eaton and Moriarty.[6] Unlike the case with some other bridgehead systems, where the cleavage of a four-membered ring that is observed may be responsible for accelerating solvolysis,[7] the products obtained from $2^+$ and $3^+$ were found to be unrearranged. Thus, in order to explain the unexpectedly rapid rate of formation of $2^+$ and $3^+$, Rüchardt and Eaton were each led to suggest nonclassical stabilization of these bridgehead ions.

In this communication we report the results of ab initio calculations on $1^+$, $2^+$, and $(CH_3)_3C^+$. When electron correlation is included, our calculations confirm that less energy is required to form $2^+$ than to form $1^+$. Evidence is presented which suggests that stabilization of $2^+$ involves cross-ring bonding to the $\beta$ carbons and concomitant delocalization of positive charge to the $\alpha$ and $\gamma$ carbons.

**Table I.** Energies (kcal/mol) Computed with the 6-31G* Basis Set at 3-21G Optimized Geometries for Formation of 1-Norbornyl Radical ($1^\bullet$) and Cation ($1^+$) and Cubyl Radical ($2^\bullet$) and Cation ($2^+$), Relative to the Energies Required for the Formation of $(CH_3)_3C^\bullet$ and $(CH_3)_3C^+$

| reaction | calculation | R: 1 | R: 2 |
|---|---|---|---|
| $RH \rightarrow R^+$ | RHF | 15.6 | 20.2 |
| $RH \rightarrow R^\bullet$ | RHF/UHF | 10.3 | 11.0 |
| $R^\bullet \rightarrow R^{+a}$ | UHF/RHF | 14.6 | 10.5 |
| $R^\bullet \rightarrow R^{+b}$ | UHF/RHF | 5.3 | 9.2 |
| $RH \rightarrow R^+$ | MP2 | 14.9 | 7.6 |

[a] Vertical radical ionization. [b] Adiabatic radical ionization. The difference between the vertical and adiabatic ionization energies for $(CH_3)_3C^+$, i.e., the energy lowering on going from the $C_{3v}$ optimized geometry of the radical to the $C_{3h}$ optimized geometry of the cation, is 11.9 kcal/mol.

Geometries were optimized with the 3-21G basis set.[8,9] Vibrational analyses showed the stationary points located to be minima. Energies at the 3-21G optimized geometries[10] were recalculated with the 6-31G* basis set,[11] both at the RHF level and with inclusion of electron correlation at the MP2 level.[12] The calculations were performed with Gaussian 86.[13] The energies obtained[10] were used to compute the energies of the reactions in Table I.

Both $1^+$ and $2^+$ are calculated to require substantially more energy to be formed from the corresponding alkanes than is $(CH_3)_3C^+$. As Table I also shows, the major reason is that the bond dissociation energy for a bridgehead hydrogen in both 1-H and 2-H is calculated to be higher than that for the tertiary hydrogen in $(CH_3)_3CH$. The predicted difficulty in forming both $1^\bullet$ [14] and $2^\bullet$,[15] relative to $(CH_3)_3C^\bullet$, is in agreement with experiment.

Despite the more highly constrained C–C–C bond angles in 2-H, its bond dissociation energy is computed to be similar to that of 1-H. The $\alpha$ hydrogens in $2^\bullet$ each have a very small spin density [0.01 versus 0.10 for each of the three equivalent hydrogens in $C_{3v}$ $(CH_3)_3C^\bullet$], and the $\alpha$ C–H bond length of 1.073 Å is actually the shortest in $2^\bullet$. Thus, C–H hyperconjugation does not appear to be very important in $2^\bullet$,[16a] which is consistent with the theoretical prediction[16] and experimental finding[17] that the $\pi$ bond in cubene is comparatively weak.

Some special stabilization for $2^+$ is suggested by the finding that, although the radical center in $2^\bullet$ is much more pyramidalized

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[1] Bartlett, P. D.; Knox, L. H. *J. Am. Chem. Soc.* **1939**, *61*, 3184.

[2] Review: Fort, R. C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1973; Vol. 4, p 1783.

[3] (a) Gleicher, G. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 582. (b) Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189. (c) Parker, W. R. L.; Watt, C. I. F.; Chary, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7121.

[4] Müller, P.; Blanc, J.; Mareda, *Chimia* **1987**, *41*, 399. Müller, P.; Mareda, J. *J. Comp. Chem.* **1989**, *10*, 863 and references cited therein.

[5] Mergelsberg, I.; Langhals, H.; Ruchardt, C. *Chem. Ber.* **1983**, *116*, 360.

[6] Eaton, P. E.; Yang, C.-X.; Xiong, Y. *J. Am. Chem. Soc.*, first of three papers in this issue. Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. K. *J. Am. Chem. Soc.*, third of three papers in this issue. Kevill, D. N.; D'Souza, M. J.; Moriarty, R. M.; Tuladhar, S. M.; Penmasta; R.; Awasthi, A. K. *J. Chem. Soc., Chem. Commun.*, submitted for publication. We thank Professors Eaton and Moriarty for communicating their results to us in advance of publication, and we thank Professor Eaton for conversations that stimulated this computational study.

[7] Wiberg, K. B.; Hess, B. A.; Ashe, A. J. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1973; Vol. 3, p 1295.

[8] Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

[9] Reoptimization of $1^+$ and $2^+$ with 6-31G* had only small effects on their geometries and energies.[10]

[10] Available as supplementary material; ordering information is given on any current masthead page.

[11] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 212.

[12] Moller, C.; Plesset, M. S. *Phys. Rev.* **1936**, *46*, 618. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *S10*, 1.

[13] Frisch, M.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; Defrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; Pople, J. A., Carnegie-Mellon University.

[14] Applequist, D. E.; Kaplan, L. *J. Am. Chem. Soc.* **1965**, *87*, 2194. Fort, R. C.; Franklin, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 5267. Humphrey, C. B.; Hodgson, B.; Pincock, R. E. *Can. J. Chem.* **1968**, *46*, 3099. Oberlinner, A.; Ruchardt, C. *Tetrahedron Lett.* **1969**, 4685. Ruchardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830. Danen, W. C.; Tipton, T. J.; Saunders, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 5186. Heine, H.-G.; Hartmann, W.; Lewis, F. D.; Lauterbach, R. T. *J. Org. Chem.* **1976**, *41*, 1907. Fort, R. C.; Hiti, J. *J. Org. Chem.* **1977**, *42*, 3968. Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

[15] Stock, L. M.; Luh, T.-Y. *J. Org. Chem.* **1978**, *43*, 3271.

[16] (a) Schubert, W.; Yoshimine, M.; Pacansky, J. *J. Phys. Chem.* **1981**, *85*, 1340. (b) Takada, T.; Dupuis, M. *Chem. Phys. Lett.* **1982**, *93*, 193. (c) Hrovat, D A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710.

[17] Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230. Homocub-4(5)-ene has also been generated and trapped: Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 7229. Schafer, J.; Szeimies, G. *Tetrahedron Lett.* **1988**, *41*, 5253.

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than that in **1**$^{\bullet}$, **2**$^{\bullet}$ has the lower vertical ionization potential. However, relaxation from the geometry of the radical to the geometry of the cation, which stabilizes **1**$^{+}$ by 21.2 kcal/mol, stabilizes **2**$^{+}$ by only 13.2 kcal/mol. The optimized bond angles at the bridgehead carbon go from 111.0° and 2 × 103.9° in **1**$^{\bullet}$ to 120.2° and 2 × 111.6° in **1**$^{+}$. The more rigid cubyl skeleton permits much less planarization at the cationic carbon in **2**$^{+}$, so that, on going from **2**$^{\bullet}$ to **2**$^{+}$, the bond angles at this carbon increase from 91.8° to only 98.3°.[18] The greater relaxation energy of **1**$^{+}$ is responsible for the finding that, at the RHF level, it is predicted to be formed from the corresponding hydrocarbon 4.6 kcal/mol more readily than **2**$^{+}$.[19]

Delocalized species in general[20] and nonclassical carbocations in particular[21] are stabilized, relative to localized classical structures, by inclusion of electron correlation. Therefore, it is not surprising that, with inclusion of electron correlation at the MP2 level, **2**$^{+}$ is selectively stabilized, so that its formation from **2**-H is now calculated to require 7.3 kcal/mol *less* energy than formation of **1**$^{+}$ from **1**-H.[22] A 3-21G vibrational analysis confirmed that **2**$^{+}$ is a true MP2 energy minimum.

C–H hyperconjugation does not appear to be very important for stabilizing **2**$^{+}$. As with **2**$^{\bullet}$, the $\alpha$ C–H bond length is the shortest in **2**$^{+}$. A Mulliken population analysis of the 6-31G* RHF wave function for **2**$^{+}$ finds the charge (0.31) at each of the $\alpha$ hydrogens to be only marginally greater than that (0.29) at each of the $\beta$ hydrogens and at the $\gamma$ hydrogen. Given the apparent unimportance of C–H hyperconjugation, it is not surprising that a degenerate 1,2-hydrogen shift in **2**$^{+}$ is calculated to have a very substantial barrier of 54.3 kcal/mol at the 6-31G* RHF level and 41.2 kcal/mol with MP2.

The population analysis reveals, surprisingly, that the $\gamma$ C–H group is about as positively charged (0.16) as each of the $\alpha$ C–H groups and more positively charged than each of the $\beta$ C–H groups (0.05). The additional finding of a positive bond order between the electron-deficient p orbital at the cationic carbon and the p orbital, aligned with it, at each of the three $\beta$ carbons suggests that some stabilization of **2**$^{+}$ comes from delocalization of the electrons in the $\alpha,\beta$ and $\beta,\gamma$ C–C bonds. The fact that this delocalization results in *three* cross-ring bonding interactions to the cationic carbon in **2**$^{+}$ is presumably responsible, at least in part, for the result that each corresponding cross-ring distance (2.100 Å with 3-21G and 2.039 Å with 6-31G* RHF optimizations) is considerably longer than that calculated for cations, like bicyclobutonium[23] and bridgehead bicyclo[*n*.1.1]alkylium,[24] in which there is only one such interaction. The relative weakness of the individual, cross-ring, bonding interactions in **2**$^{+}$ is probably why each of the six, $\alpha,\beta$ C–C bonds lengthens by only about 0.02 Å on formation of **2**$^{+}$ from **2**-H and why the length of the three $\beta,\gamma$ bonds remains almost unchanged.

On the basis of the results of the population analysis of **2**$^{+}$, the presence of $\sigma$ electron withdrawing substituents at the $\alpha$ or $\gamma$ carbons would be expected to destabilize the carbocation more than at the $\beta$ carbons. However, because the $\gamma$ C–H bond lies along the axis of the cylindrically symmetrical LUMO of **2**$^{+}$, $\pi$-donor substituents at the $\gamma$ carbon should not be effective at stabilizing the carbocation. Computational tests of these qualitative predictions are in progress. Experimentally, Eaton and Moriarty have already found that electron-withdrawing substituents at the $\gamma$ carbon greatly retard the rate of carbocation formation and that the presence of a methyl group—a $\pi$ but not a $\sigma$ donor—at this carbon atom also has a small, rate-retarding effect.[6]

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**Registry No.** 2-Methylpropane, 75-28-5; *tert*-butyl cation, 14804-25-2; *tert*-butyl radical, 1605-73-8; bicyclo[2.2.1]heptane, 279-23-2; bicyclo-[2.2.1]heptyl cation, 21898-87-3; bicyclo[2.2.1]heptyl radical, 2697-23-6; cubane, 277-10-1; cubyl cation, 125665-92-1; cubyl radical, 67151-55-7.

**Supplementary Material Available:** Optimized geometries and energies for the hydrocarbons, radicals, and cations discussed in the paper (26 pages). Ordering information is given on any current masthead page.

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[18] The pyramidal geometry at this carbon is presumably responsible for the finding that its chemical shift, $\delta$ 384.9, relative to methane, is calculated to be unusually large. We are indebted to Professor Paul Schleyer for performing IGLO chemical shift calculations on **2**$^{+}$ and communicating the results to us.

[19] The hydrocarbons appear to be satisfactory reference compounds, since at the 6-31G* RHF level formation of **2**$^{+}$ from **2**-OH is calculated to require 20.7 kcal/mol more energy than formation of $(CH_3)_3C^+$ from $(CH_3)_3COH$. This value agrees well with the 20.2 kcal/mol energy difference computed when the hydrocarbons are used as the reference compounds.

[20] For examples and a discussion, see: Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783 and references therein.

[21] For examples, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; pp 379–396. Raghavachari, K.; Haddon, R. C.; Schleyer; P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 5915. Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185. Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300.

[22] The MP2 relaxation energies of −22.2 kcal/mol for **1**$^{+}$, −13.9 kcal/mol for **2**$^{+}$, and −12.6 kcal/mol for $(CH_3)_3C^+$ are all very close to those computed at the RHF level. Thus, the selective stabilization of **2**$^{+}$ by inclusion of electron correlation cannot be attributed to an increase in the magnitude of its relaxation energy. In fact, formation of **2**$^{+}$ from **2**-H is calculated at the MP2 level to require 15.6 kcal/mol less energy than formation of **1**$^{+}$ from **1**-H when the energies of the cations are each computed at the geometry of the corresponding radical.

[23] McKee, M. L. *J. Phys. Chem.* **1986**, *90*, 4908. Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7325. Saunders, M.; Laidig, K.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652.

[24] Della, E. W.; Gill, P. M. W.; Schiesser, C. H. *J. Org. Chem.* **1988**, *53*, 4354.

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## Solvolyses of Cubyl Triflates. The Cubyl Cation[†,1]

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Nucleophilic substitution reactions upon cubyl iodide are fundamentally limited by the structural impossibility of an $S_N2$ backside attack and by the assumed instability of the cubyl cation in an $S_N1$ solvolysis. In effect, in recent synthetic work,[2] we and others have circumvented these two pathways by using an oxidative nucleophilic displacement along the lines of the work of Wiberg et al.,[3] Kropp et al.,[4] and Zefirov et al.[5] While the exact nature of hypervalent iodine in oxidative displacement is not totally clear,[2] this work afforded us the series of 4-substituted triflates **2a–f**,[6]

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[†] Dedicated to Professor Paul von Rague Schleyer on the occasion of his 60th birthday.

[1] A preliminary report of this work was made: Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. K. Presented at the 198th National Meeting, of the American Chemical Society, Miami Beach, FL, Sept 10–15, 1989; paper ORGN 18.

[2] Moriarty, R. M.; Khosrowshahi, J. S. *Synth. Commun.* **1989**, *19*, 1395. See also: Eaton, P. E.; Kunkle, G. T. *Tetrahedron Lett.* **1986**, *27*, 6053.

[3] Wiberg, K. B.; Pratt, W. E.; Matturo, M. G. *J. Org. Chem.* **1982**, *47*, 2720.

[4] Davidson, R. I.; Kropp, P. J. *J. Org. Chem.* **1982**, *47*, 1904.

[5] Zefirov, N. S.; Zdhankin, V. V.; Kozmin, A. S. *Tetrahedron Lett.* **1986**, 1845.

[6] Synthesis of cubyl triflates: In a typical experiment, a mixture of cubyl iodide (1 mmol), $(C_6H_5IO)_n$ (3 mmol), and $(CH_3)_3SiOTf$ (3 mmol) in dry $CH_2Cl_2$ (50 mL) was stirred at room temperature for 1 h to several days, depending on the $C_4$ group: $H < CH_3 < CO_2CH_3 <$ Br, I, Cl. After the usual workup, the product was purified by flash chromotography (using pentane) or microdistillation under vacuum, to produce the pure compound in 50–60% yield.

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