4216 *J. Org. Chem.* **1997,** *62,* 4216−4228

# Why the Classical and Nonclassical Norbornyl Cations Do Not Resemble the 2-*endo*- and 2-*exo*-Norbornyl Solvolysis Transition States[1,†]

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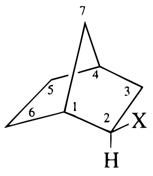
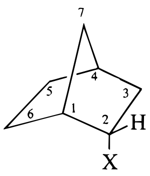
*Received July 15, 1996*[⊗]

In order to analyze the solvolysis behavior of epimeric norbornyl derivatives, the dissociative mechanisms of protonated 2-*exo*- (**1**, $X = OH_2^+$) and 2-*endo*-norbornanol (**2**, $X = OH_2^+$), 1-methyl-2-*exo*- (**7**) and 2-*endo*-norbornanol (**8**), and 1-phenyl-2-*exo*- (**9**) and 2-*endo*-norbornanol (**10**) were studied *ab initio* at the B3LYP/6-311+G*//B3LYP/6-31G* level. In agreement with the experimental solvolysis data, the activation energy (including the 1.2 kcal mol$^{-1}$ ground state energy difference) for dissociation of *exo*-**1** ($X = OH_2^+$) is 3.7 kcal mol$^{-1}$ lower than that of *endo*-**2** ($X = OH_2^+$). This value is much smaller than the 14 kcal mol$^{-1}$ energy difference favoring the isolated nonclassical (**3**) over the classical (**5**) 2-norbornyl cation. That the rate acceleration reflects only a small part of the driving force available poses a general interpretative problem in neighboring group participation. Winstein's hypothesis, that "bridging lags behind ionization" is *not* the full explanation for this discrepancy. Brown's hypothesis, that there is "steric hindrance to ionization from the (norbornyl) *endo* face", is not correct as the interaction of the (partially positively charged) *endo*-hydrogen (C6) and the leaving group is *attractive* in the transition state. Although the structure of the $C_7H_{11}^+$ moiety in the *exo*-transition state is unsymmetrical, its energy is only 1.3 kcal mol$^{-1}$ higher than that of the fully relaxed nonclassical norbornyl cation (**3**). The norbornyl cation moiety in the 2-*endo* transition structure (also computed by removing the water molecule and retaining the $C_7H_{11}^+$ geometry) is 4.3 kcal mol$^{-1}$ more stable than the classical 2-norbornyl cation but 8.8 kcal mol$^{-1}$ less stable than the fully bridged ion. Hence, the changes in geometry and charge distribution in the solvolysis transition structures reduce the energy difference of the classical and nonclassical cation moieties in the *endo* and *exo* transition structures to 7.5 kcal mol$^{-1}$. This is reduced further by the stronger leaving group interaction in the 2-*endo* over the 2-*exo* transition structure. The leaving group interaction with the developing carbocation in the 2-*endo*-norbornyl transition structure is stronger than in the 2-*exo*-transition structure. This difference (which exemplifies the general behavior of participating systems) arises since the stabilizing interactions of the neighboring group and of the leaving group must *compete*. Consequently, the effectiveness of *both* the neighboring group and the leaving group interactions is reduced relative to anchimerically unassisted solvolysis, and only a fraction of the potential driving force is reflected in the stabilization of the transition structure of participating systems. This is shown even more dramatically by the very modest effect (which was confirmed computationally) of a 1-methyl or a 1-phenyl substituent on the rate of 2-*exo*-norbornyl solvolyses (less than 100-fold acceleration), despite the huge increase in driving force.

## Introduction



*exo* (**1**)



*endo* (**2**)

Winstein and Trifan's 1949 observation of the distinctly different behavior of 2-*exo*- (**2**) and 2-*endo*-norbornyl (**3**) derivatives on solvolysis[3] eventually led to the heated controversy, *The Nonclassical*[4] *Ion Problem* (the title of H. C. Brown's book).[5,6] Winstein and Trifan's (WT) pioneering study[3] revealed that the titrimetric rate of solvolysis of 2-*exo*-norbornyl brosylate (**1**, X = *p*-bromobenzenesulfonate (pOBs), a good leaving group) in acetic acid is 350 times faster than that of the 2-*endo* isomer (**2**, X = pOBs). This rate ratio is abnormally large, compared with the behavior of epimers of other cyclic

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[†] This paper is dedicated to Paul D. Barlett for his seminal contributions to physical organic chemistry.

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

(1) This paper was presented at the KISPOC VII in Japan, 1995.

(2) (a) University of Georgia. (b) Universität Erlangen-Nürnberg.

(3) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1949**, *71,* 2953; **1952**, *74,* 1147, 1154.

(4) A carbocation is nonclassical if it cannot be described adequately by a single Lewis structure.[5] See: Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73,* 3542.

(5) Brown, H. C., with comments by Schleyer, P. v. R. *The Nonclassical Ion Problem*; Plenum: New York, 1977. For other reviews, see refs 6 and 12.

(6) (a) Lenoir, D.; Apeloig, Y.; Arad, D.; Schleyer, P. v. R. *J. Org. Chem.* **1988**, *53,* 661; this paper is the latest available review on the norbornyl solvolysis literature. (b) Brown, H. C. *Acc. Chem. Res.* **1986**, *19,* 34. (c) Barkhash, V. A. *Topics in Current Chemistry*; Springer: Berlin, 1984; Vol. 116/117, pp 1−249. (d) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1983**, *105,* 3571. (e) Lenoir, D. *Nachr. Chem. Tech. Lab.* **1983**, *31,* 889. (f) Walling, C. *Acc. Chem. Res.* **1983**, *16,* 448. (g) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1982**, *104,* 7105. (h) Lyerla, J. R.; Yannoni, C. S.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15,* 208. (i) Kirmse, W. *Topics in Current Chemistry*; Springer: Berlin, 1979; Vol. 80, p 128. (j) Olah, G. A. *Topics in Current Chemistry*; Springer: Berlin, 1979; also see ref 11.

S0022-3263(96)01338-2 CCC: $14.00

**Scheme 1**

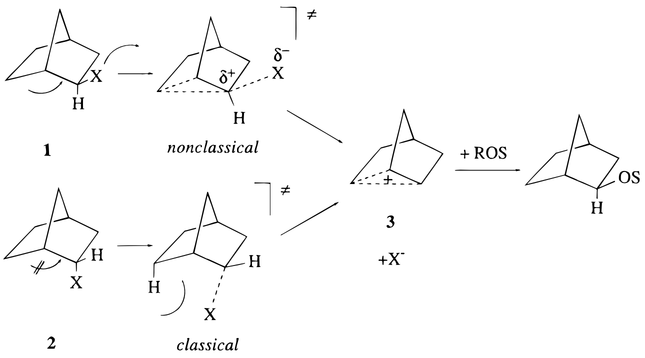
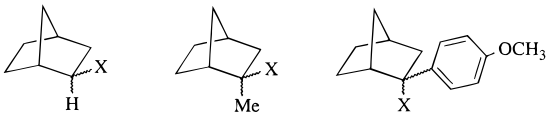


**Chart 1**



**350**[5] **885**[8] **285**[9]

systems. Moreover, the *exo*/*endo* ratio is even larger when the rates of *racemization* were compared. Starting with optically active 2-*exo*-norbornyl brosylate, the *polarimetric* rate exceeded the acetolysis rate (measured titrimetrically) by a factor of $10^{3.5}$ (later revised to $10^{4.6}$).[5] While the acetolysis of optically active 2-*endo*-norbornyl brosylate (**2**, X = pOBs) also yielded racemized (>99.9%) 2-*exo*-norbornyl acetate, the polarimetric and titrimetric rates were equal. Hence, the *exo* reaction proceeds faster via an effectively symmetrical ion pair intermediate which could undergo internal return before product formation.[7] Only *exo* products (generally ≥ 99.9%) are obtained from **1** and **2**.

The alternative possibility of two rapidly equilibrating norbornyl cations or ion pairs did not, in WT's view, account for the large *exo*/*endo* rate ratio. This was attributed to the "anchimeric assistance" involving the well-oriented C2−C6 bond during the *exo* but not the *endo* solvolysis. WT argued that this neighboring group participation in **1** leads to a delocalized "nonclassical" transition structure and then to the symmetrical nonclassical norbornyl cation or ion pair. In contrast, solvolysis of **2** was suggested to proceed via a "classical" transition structure in the rate-limiting step, which then collapses to the same bridged ion from which the products derive.

Brown advanced a fundamentally different interpretation.[5] He pointed out that the *exo*/*endo* ratios of tertiary norbornyl systems (with 2-methyl and even 2-anisyl substituents) were also large, despite the expected classical character of tertiary cation intermediates.

Brown also called attention to many reactions of norbornyl systems which exhibit large *exo*/*endo* ratios (e.g., epoxidation of norbornene) but could not involve bridged transition states or even, in some cases, cations.[5] Large *exo*/*endo* ratios, in his view, more likely are steric in origin. Brown argued that **2** might suffer from steric hindrance to ionization, *i.e.*, in the solvolysis transition state, the leaving group would collide with the *endo*-hydrogen in the 6-position.[10] According to Brown, the *exo* solvolysis rate is "normal", while the *endo* solvolysis is inhibited due to this steric hindrance.

This proved not to be the correct interpretation. A comparison of the solvolysis rates of various secondary substrates in non-nucleophilic solvents showed that the 2-*endo*-norbornyl solvolysis rate is quite "normal" while that of the *exo* isomer is clearly exceptional.[11]

Olah's discovery of superacid media[12] enabled the direct spectroscopic observation of the norbornyl cation (**3**),[13] first in 1964 by Schleyer, Watts, Fort, Comisarow, and Olah[13a] and by Saunders, Schleyer, and Olah.[13b] The structure of the ion itself became part of the debate. Although the geometry of **3** is still not known experimentally,[14] ingenious experimental methods[15] in combination with high-level *ab initio* computations[16] finally established its symmetrically bridged structure **3** beyond reasonable doubt.[12] While the stable ion structure no longer is controversial, the full interpretation of the norbornyl solvolysis behavior, the nature of the ion pair intermediate, and the nature of the transition states as for product formation, as well as those for *exo* and *endo* solvolysis, is far from established.[6]

Thus, the most recent very extensive studies of the substitution effects on 2-norbornyl solvolysis rates in the 1980s led Grob *et al.*[17] to question whether "the solvolytically generated norbornyl cation is better represented by the asymmetrically bridged structure". We stress that the structure of stable nonclassical carbocations does *not*

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[7] The first good evidence for such ion pair intermediates in related terpene rearrangements had been presented by Nevell, T. P.; deSalas, E.; Wilson, C. L. *J. Chem. Soc.* **1939**, 1188.

[8] Ikegami, S.; Van der Jagt, D. L.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 7124.

[9] Brown, H. C.; Takeuchi, K. *J. Am. Chem. Soc.* **1968**, *90*, 2691.

[10] Brown, H. C.; Chloupek, F. J. *J. Am. Chem. Soc.* **1963**, *85*, 2322.

[11] (a) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466. (b) Bentley, T. W.; Carter, G. E. *J. Org. Chem.* **1983**, *48*, 579.

[12] For a historical account, see: Olah, G. A. *Angew. Chem.* **1995**, *107*, 1519. Also see: (a) Olah, G. A., Schleyer, P. v. R., Eds. *Carbonium Ions*; Wiley-Interscience: New York, 1968−1976; Vol. I−IV. (b) Olah, G. A. *Carbocations and Electrophilic Reactions*; Verlag Chemie: Weinheim, 1974. (c) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985. (d) Olah, G. A.; Molnár, A. *Hydrocarbon Chemistry*; Wiley: New York, 1995. (e) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987.

[13] (a) Schleyer, P. v. R.; Watts, W. E.; Fort, R. C., Jr.; Comisarow, M. B.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 4195. (b) Saunders, M.; Schleyer, P. v. R.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 5680. (c) Olah, G. A.; White, A. M.; DeMember, J. R.; Commeyras, A.; Lui, C. Y. *J. Am. Chem. Soc.* **1970**, *92*, 4627. (d) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1982**, *104*, 7105. (e) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440.

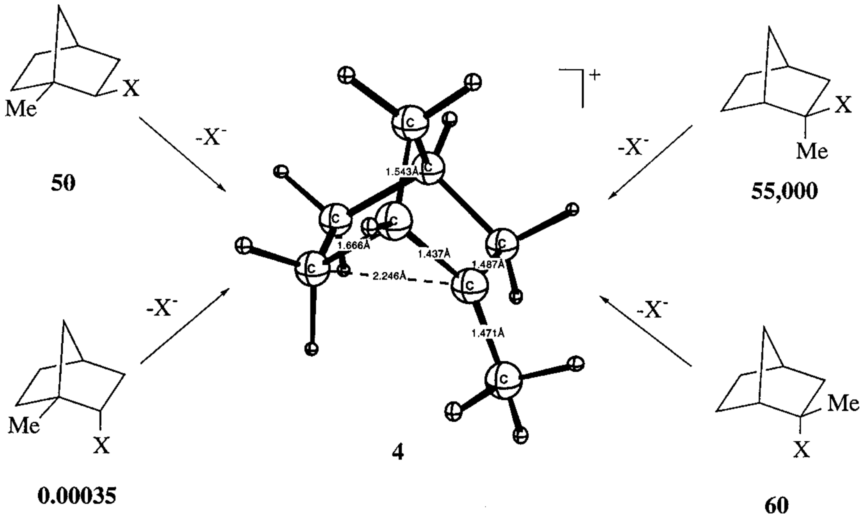
[14] The X-ray structure of the 1,2,4,7-*anti*-tetramethyl-2-norbornyl cation shows only unsymmetrical bridging, with 1.409(9) Å $C_1-C_2$, 1.699 Å $C_1-C_6$, and 2.113(9) Å $C_2-C_6$ distances; see: Laube, T. *Angew. Chem.* **1986**, *98*, 368.

[15] (a) Olah, G. A.; Mateescu, G. D.; Wilson, L. A.; Gross, M. H. *J. Am. Chem. Soc.* **1970**, *92*, 4627. (b) Olah, G. A.; Mateescu, G. D.; Riemenschneider, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2529. (c) Johnson, S. A.; Clark, D. T. *J. Am. Chem. Soc.* **1988**, *110*, 4112. (d) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 6867. (e) Saunders, M.; Johnson, C. S., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 4401. (f) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 7380.

[16] (a) Sieber, S.; Buzek, P.; Schleyer, P. v. R.; Koch, W.; Carneiro, J. W. de M. *J. Am. Chem. Soc.* **1993**, *115*, 259. (b) Schleyer, P. v. R.; Sieber, S. *Angew. Chem.* **1993**, *32*, 1606 and earlier references cited therein. (c) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 1527. (d) Koch, W.; Liu, B.; DeFrees, D. J.; Sunko, D. E.; Vancik, H. *Angew. Chem.* **1990**, *102*, 198. (e) Raghavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 5915.

[17] (a) Flury, P.; Grob, C. A.; Wang, G. Y.; Lennartz, H.-W.; Roth, W. R. *Helv. Chim. Acta* **1988**, *71*, 1017. (b) Bielmann, R.; Fuso, F.; Grob, C. A. *Helv. Chim. Acta* **1988**, *71*, 312. (c) Altmann-Schaffner, E.; Grob, C. A. *Helv. Chim. Acta* **1987**, *70*, 43. (d) Fuso, F.; Grob, C. A.; Sawlewicz, P.; Yao, G. W. *Helv. Chim. Acta* **1986**, *69*, 2098. (e) Grob, C. A. *Helv. Chim. Acta* **1983**, *66*, 3139.

**Scheme 2**

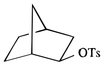
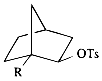
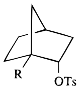
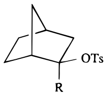


explain the intricacies of their solvolysis behavior.[18] For instance, 1- and 2-methyl-2-*exo*- and -*endo*-norbornyl derivatives (Scheme 2) give the *same* cation intermediate (both in solvolysis and in stable ion media) but exhibit very different (over $10^8$) reaction rates. Obviously, little can be learned about the nature of the *four different transition states* from the structure of the single tertiary cation.

Indeed, a host of puzzling problems involving "neighboring group participation" from the 1950s and 1960s remain unsolved despite the numerous investigations of many of the leading physical organic chemists. Since many ions are not stable in superacidic media, much of our knowledge of carbocation chemistry still derives from solvolysis studies. Hence, we seek to clarify the behavior of these positively charged reactive intermediates particularly in weakly nucleophilic solvolysis solvents.[19]

To what extent is carbon bridging[20] involved in the 2-*exo*-norbornyl solvolysis transition state? Not very much, according to other evidence.[5,17] Rather than being quite large, the 1600 polarimetric (racemization) *exo*/*endo* rate ratio[21] of the parent secondary 2-norbornyl system is, in reality, much smaller than the $10^8$ *exo* ratio expected on the basis of the driving force available (see below). Despite the even larger driving forces associated with rearrangement to the much more stable tertiary ions, carbocation-stabilizing substituents in the 1-position, *e.g.*, alkyl, aryl, and methoxy, increase the *exo* rates and *exo*/*endo* ratios to remarkably small extents (Table 1, see Scheme 2),[5] even though the tertiary ions which ensue are highly stabilized. "The results suggest that the transition state is only modestly along the reaction coordinate toward the tertiary cation."[15] This emphasizes that the nature of stabilized tertiary 2-norbornyl cations in superacids (which have been established by a number of experimental[5−15] and theoretical methods[16] in conjunction) does *not* explain the *general* 2-norbornyl solvolysis behavior.

**Table 1. Comparison of Solvolysis Rates for 1-Substituted 2-Norbornyl Tosylates vs 2-*exo*-Norbornyl Tosylate[5]**

| R |  |  |  |  |  |
|---|---|---|---|---|---|
| Methyl | 1.0 | 0.004 | **50** | 0.004 | $6 \cdot 10^4$ |
| Phenyl | 1.0 | 0.004 | **3.9** | 0.002 | $3 \cdot 10^8$ |
| p-Anisyl | 1.0 | 0.004 | **7.8** | 0.003 | $5 \cdot 10^{11}$ |

The symmetrically bridged 2-norbornyl cation (**3**) is considerably more stable than other secondary carbocations,[11] as well as all other bicyclic $C_7H_{11}^+$ isomers.[16,22] The "classical" 2-norbornyl cation model (**5**) is not even a high-lying minimum, as the only stationary point in the region is a transition structure for rearrangement to the norpinyl (2-bicyclo[3.1.1]heptyl) system.[16,23] The rather reliably estimated relative energy (MP4SDQ(full)/6-31G*//MP2(full)/6-31G*) of **5** is 13−14 kcal mol$^{-1}$ about that of **3**,[16b,24] in agreement with our earlier crude extrapolation based on the energy of **3** at different levels of theory.[16e]

The vertical ionization potential of the 2-norbornyl radical (*i.e.*, the corresponding energy of the cation computed using the optimized geometry of the radical) provides another estimate of the relative energy of a good

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[18] This contradicts the common assumption, reflected in the comment of a referee: "Chemists know well that in any reaction, including solvolysis, the structure of the intermediate is a most important guiding post for the nature of the transition state." This has long been known not to be the case for 2-*endo*-norbornyl solvolysis (see, *e.g.*, Olah, G. A. *Acc. Chem. Res.* **1975**, *8*, 413), and we show that this is *not* the case for 2-*exo*-norbornyl solvolysis as well.

[19] (a) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1. (b) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658. (c) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

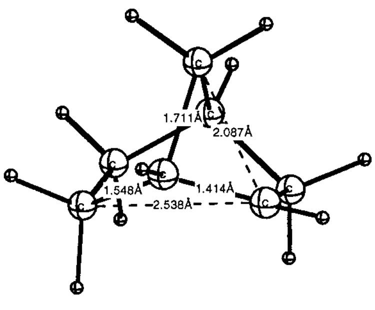
[20] Bridging in the norbornyl cation system implies movement of C6 from C1 toward C2; the C1−C6 distance lengthens, and the C2−C6 (as well as the C1−C2) bond shortens. These changes, of course, are accompanied by delocalization of the C1−C6 electron density. The important consequences of a symmetrical bridge, *e.g.*, in the 2-norbornyl cation, include the loss of chirality. Schleyer and Olah have stressed the continuum of bridging possibilities in carbocations: Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

[21] Expressed in terms of free energy (Goering−Schewene) diagrams, which correct for the *ca.* 1 kcal mol$^{-1}$ greater stability of *exo* over *endo* ground states; the *exo* solvolysis transition state (corrected for internal return) is *ca.* 5−6 kcal mol$^{-1}$ lower in energy than the *endo*-TS; see: Goering, H. L.; Schewene, C. B. *J. Am. Chem. Soc.* **1965**, *87*, 3516.

[22] Sieber, S. Dissertation, Erlangen, 1994.

[23] Kirmse, W.; Minkner, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 385.

[24] For comparison with our level used throughout this paper, we computed the energy difference at B3LYP/6-311+G* and found 13.1 kcal mol$^{-1}$. Note that a classical ($C_1$) norbornyl cation minimum does not exist even at the HF/6-31G* level.



**5** ($C_1$, a "classical" cation model, a TS at B3LYP/6-31G*)

classical ion model **5** vs **3**. The relative energy, 14.7 kcal mol$^{-1}$ (B3LYP/6-311+G*//B3LYP/6-31G*; Tabel 3), agrees well with the other estimates.[16]

By comparing nucleophilically unassisted solvolysis rates for a variety of secondary and tertiary systems to the directly measured heats of ionization in "superacid" media, Arnett, Petro, and Schleyer[25] showed in 1979 that *ca.* 90% of the "carbocation character" is developed in the solvolysis transition states. The same conclusion was reached by Müller *et al.*[26] by relating the experimental gas phase $D_0$ ($R^+-Br^-$) heterolytic bond dissociation energies with solvolysis rates. On this basis, the energy difference between the 2-*exo*- and 2-*endo*-norbornyl solvolysis transition states is expected to be about 12 kcal mol$^{-1}$ (0.9 × 13.6 kcal mol$^{-1}$). Why is only a fraction of this (*ca.* 4−6 kcal mol$^{-1}$; 33−50% rather than 90%) observed experimentally? Why, as mentioned above (Scheme 2), do the carbocation-stabilizing substituents at the 1-position have such remarkably small effects?

This troublesome discrepancy between the stability of the carbocation intermediates and the energies of solvolysis transition states is apparent not only in the 2-norbornyl but also in many other participating systems, where even larger driving forces are not reflected in the degree of anchimeric (neighboring group) assistance.[5]

Winstein was well aware of this problem, and his rationalization, "bridging lags behind ionization",[27] is now subjected to the detailed scrutiny afforded by modern *ab initio* computations. Even if Winstein was correct, the reasons for the "lagging bridging" have never been clarified in detail. While much is known experimentally and theoretically about the nature of carbocations,[12] detailed descriptions of solvolysis transition structures leading to nonclassical ions and from these ions to the products are *not available*.[28] These are the main focus of the present paper.

Another possible rationalization was excluded recently: the solvation energies of "classical" and "nonclassical" ions do *not* differ significantly.[29] The differences in free energies of hydration ($\Delta\Delta G_{hyd}$) for the fixed MP2-(full)/6-31G* geometries of the classical (**5**) and nonclassical (**3**) 2-norbornyl cations were computed using statistical perturbation theory[30] as implemented in the BOSS program.[31] However, the $\Delta\Delta G_{hyd}$ is only 0.7−0.8 kcal mol$^{-1}$ in favor of **5**, due to considerable charge delocalization. Consequently, a full explanation of the 2-*exo*- and 2-*endo*-norbornyl solvolysis rate ratios requires a detailed analysis of the solvolysis transition states.

## Methods

The study reported in this paper was preceded by *very extensive investigations of the theoretical levels as well as the most appropriate leaving group models*. Although the *details* of the results vary somewhat, the general conclusions are the same. We have chosen what we consider to be the best practicable level for presentation in this paper.

Geometries of all stationary points were optimized using self-consistent-field (SCF) and density functional analytic gradient methods. The Lee−Yang−Parr (LYP)[32] three-parameter exchange-correlation functionals including Becke's[33] nonlocal gradient exchange corrections were employed as implemented in the Gaussian program package.[34] Residual Cartesian and internal coordinate gradients for the stationary points were always less than $10^{-5}$ au. Harmonic vibrational frequencies were computed by analytic second-derivative methods.[35] Two standard basis sets were employed: 6-31G* for geometry optimizations and 6-311+G* for energies.

The diffuse functions in the latter should reduce the basis set superposition errors (BSSE),[36] which (as a referee suggested) may, however, still be significant. An estimation of the BSSE using the counterpoise method[37] gives BSSEs in the range of 1−2 kcal mol$^{-1}$ for the weakly bound species and transition structures considered here (*e.g.*, 1.2 kcal mol$^{-1}$ for the nonclassical 2-nornornyl cation−water complex **6**; 1.7 kcal mol$^{-1}$ for $TS_{exo}$). Thus, the differential error among the different species is around 1 kcal mol$^{-1}$, which falls well within the expected accuracy of about 2 kcal mol$^{-1}$ of the level of theory used here. Very highly correlated (*e.g.*, CCSD(T)) methods in conjunction with very large basis sets would be needed to increase the accuracy significantly. This is, however, currently computationally not feasible. It is not clear to us how the BSSE is composed in hybrid Hartree−Fock procedures such as B3LYP, *i.e.*, whether the BSSE in the HF part is alleviated or increased by the subsequent DFT treatment. Thus, we have not corrected our absolute energies for BSSE. A systematic study on BSSE in DFT would be highly welcomed.

**Choice of Theoretical Level.** Even though the classical 2-norbornyl cation (**5**) is not a stationary point at HF/6-31G*

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[25] Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522; see also ref 11.

[26] Müller, P.; Milin, D.; Feng, W. Q.; Houriet, R.; Della, E. W. *J. Am. Chem. Soc.* **1992**, *114*, 6169. A very recent study reports a smaller slope (0.7) for a plot of the Gibbs free energy *changes* of the deprotonation reactions of substituted cumyl cations in solution and in the gas phase; see: Richards, J. P.; Jagannadham, V.; Amyes, T. L.; Mishima, M.; Tsuno, Y. *J. Am. Chem. Soc.* **1994**, *116*, 6706. A slope of 0.52 for formolysis of allyl chlorides vs the heats of deprotonation of the cation was reported by Mayr, H.; Förner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 6032.

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**Table 2. Absolute (au) and Relative Energies (kcal mol$^{-1}$) of 2-Norbornyl Derivatives and Related Species at HF and DFT Levels of Theory**

| | HF/6-31G* | | | B3LYP/6-31G* | | | B3LYP/6-311+G* | |
|---|---|---|---|---|---|---|---|---|
| species | | +ZPVE (×0.91) | relative | | +ZPVE | relative | | relative |
| **1** (X = $OH_2^+$) | 347.23585 | 118.5 | 0.0 | 349.50107 | 121.3 | 0.0 | 349.57931 | 0.0 |
| **2** (X = $OH_2^+$) | 347.23381 | 118.8 | 1.3 | 349.49811 | 121.7 | 1.9 | 349.57734 | 1.2 |
| $TS_{exo}$ | 347.22899 | 114.8 | 4.3 | 349.49103 | 117.7 | 6.3 | 349.57488 | 2.8 |
| $TS_{endo}$ | 347.22501 | 115.8 | 5.5[a] | 349.48593 | 118.5 | 7.6[a] | 349.56884 | 5.3[a] |
| **6** | 347.22944 | 115.2 | 4.0 | 349.49392 | 118.1 | 4.5 | 349.57791 | 0.9 |
| **7** | 386.27308 | 135.3 | 0.0 | 388.81884 | | 0.0 | 388.90597 | 0.0 |
| **8** | 386.27171 | 135.5 | 0.7 | 388.81610 | | 1.5 | 388.90301 | 1.9 |
| $TS_{me\text{-}exo}$ | 386.27184 | 132.8 | 0.8 | 388.81504 | | 2.5 | 388.90560 | 0.2 |
| $TS_{me\text{-}endo}$ | 386.26354 | 132.6 | 5.1[a] | 388.80490 | | 7.0[a] | 388.89491 | 5.1[a] |
| **9** | | | | 580.56516 | | 0.0 | 580.69043 | 0.0 |
| **10** | | | | 580.55783 | | 4.6 | 580.68375 | 4.2 |
| $TS_{ph\text{-}exo}$ | | | | 580.55294 | | 7.7 | 580.68403 | 4.0 |
| $TS_{ph\text{-}endo}$ | | | | 580.54052 | | 10.9[a] | 580.66958 | 8.9[a] |

[a] Relative to the corresponding *endo* ground state.

(all optimizations lead to **3**), this level is not appropriate for our purposes. The importance of electron correlation in describing the delocalized bonding in carbocations is well established. While MP2[38] computations often reproduce experimentally known carbocation structures, energies, and chemical shifts very well,[16] electron correlation effects tend to be overemphasized somewhat, and nonclassical bridged structures may be favored to too great an extent. A case in point is the 1,2-dimethylnorbornyl cation, a closely related system. While NMR data show this ion to be unsymmetrical ($C_1$ point group),[39] MP2/6-31G* favors the symmetrical $C_s$ structure. B3LYP/6-31G*, however, gives an unsymmetrical minimum (favored by 1 kcal mol$^{-1}$ over the $C_s$ transition structure; the experimental NMR barrier in superacid media is too small to measure but probably also is around 1 kcal mol$^{-1}$). The B3LYP/6-31G* geometries[40] of the 1,2-dimethyl- as well as the 1,2,4,7-*anti*-tetramethyl-2-norbornyl cation resemble the X-ray structure of the latter closely.[14] The classical 2-norbornyl cation model (**5**), a transition structure for rearrangement into the norpinyl system, has a geometry at B3LYP/6-31G* quite similar to that at MP2/6-31G* (see above).

The final level we have chosen (unless noted otherwise),[41] B3LYP/6-311+G*//B3LYP/6-31G*,[42] reproduces cation−water complexation energies satisfactorily. For instance, the dissociation energy ($D_o$) of protonated *tert*-butyl alcohol ($C_4H_9{-}OH_2^+$) is 11.0 kcal mol$^{-1}$ at this level, without BSSE corrections (expt: 11.2).[43] Both $D_o$(HF) = 9.2 kcal mol$^{-1}$ and $D_o$(MP2) = 13.5 kcal mol$^{-1}$ have larger errors.

**Choice of the Computational Solvolysis Model: The Leaving Group.** "Solvolysis" denotes the overall reaction of a substrate with a solvent, but "solvation" need *not* be an essential feature (note our Monte-Carlo simulation results,[29] described above). The nucleophilically unassisted character of both 2-*exo*- and 2-*endo*-norbornyl solvolysis was established early.[11,19] The rate-determining step involves the generation of a carbocation intermediate by the departure of a "leaving group" (*i.e.*, an anion of a reasonably strong acid). As heterolytic bond cleavages are difficult to model computationally in the absence of solvent stabilization, we have employed positively charged substrates where the leaving groups are neutral molecules (eq 1).[44] Indeed, Ingold's very first $S_N1$ paper[45] employed an ammonium ion substrate ($RNH_3^+$; ammonia as leaving group).

$$R{-}X^+ \rightarrow R^+ + X \qquad (1)$$

We first explored the behavior of a number of leaving group candidates, X = $N_2$, $NH_3$, $H_2O$, HF, HCl, LiF, and LiCl, computationally, but many of these proved not to be suitable. $RFH^+$, $RClH^+$, and $RN_2^+$ simply dissociated exothermically into weakly bound complexes on optimization, without involving (enthalpic) transition structures. Due to the high proton affinity of ammonia, an attempted transition state optimization of $RNH_3^+$ gave norbornene and the ammonium ion (*i.e.*, elimination). We found that water and lithium fluoride leaving groups are most suitable with respect to geometries and energies of the ground and transition states,[46] and both led to similar qualitative conclusions. Water is our preferred leaving group model, *e.g.*, to describe not only the heterolytic bond cleavage of a protonated alcohol or an ester[21] but *also the reaction of solvent leading to product*. Note that protonated acetates have been used experimentally as leaving groups and give the same overall results, *e.g.*, as arenesulfonates.[21]

The carbon−oxygen bond was chosen as the reaction coordinate in the preliminary search for the transition structures. As these converge only slowly owing to the flatness of the potential energy hypersurfaces, it is more efficient to probe the general feature by stepwise procedures first.[47] Standard transition structure search routines were then used to refine

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(38) Hehre, W. J.; Radom, L.; Pople, J. A.; Schleyer, P. v. R. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons, Inc.: New York, 1986. Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Binkley, J. S.; Pople, J. A. *Int. J. Quant. Chem.* **1975**, *9*, 229. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quant. Chem.* **1976**, *S10*, 1.

(39) Laube, T. *Helv. Chim. Acta* **1994**, *77*, 943.

(40) Schleyer, P. v. R.; Maerker, C. *Pure Appl. Chem.* **1995**, *67*, 755. See also: Schleyer, P. v. R.; Maerker, C.; Buzek, P.; Sieber, S. Accurate Carbocation Structures: Verification of Computed Geometries by NMR, IR, and X-Ray Diffraction. In *Stable Carbocations*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; Wiley: New York, 1997.

(41) It is noteworthy that the HF/6-31G* + ZPVE level reproduces the same qualitative features of the geometries, *i.e.*, $TS_{exo}$ at this level is *not* fully bridged, and the difference in activation energies is 2.5 (+ZPVE = 3.5) kcal mol$^{-1}$ (Table 2).

(42) Zero-point vibrational energy (ZPVE) corrections were not taken into account due to the flatness of the potential energy surfaces. In such cases, the harmonic approximation no longer is valid and would lead to an incorrect picture. This point can be explained as follows. The ZPVE equals $1/2\sum(h\nu_i)$, where $\nu_i$ are the $3N - 6$ vibrational frequencies of the molecule. Only $3N - 7$ (one mode is imaginary and is not counted) vibrations are summed into the ZPVE for a transition structure, leading to a small error if the activation barrier on the potential energy surface (PES) is sufficiently high, and the absolute value of the imaginary vibration is small. For our flat potential energy surfaces, however, this precondition is not met as a strong bond (C−O) is broken (correlating to a high $\nu_i$), leading to a large change in the ZPVEs for the ground vs the transition structure. For completeness, we have given the ZPVEs in Table 2; Figure 2 also contains the relative energies for the ground states corrected for ZPVE in parentheses.

(43) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

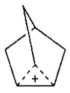
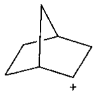
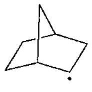
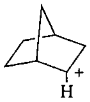
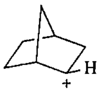
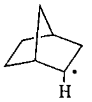
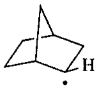
(44) Yamataka, H.; Ando, T.; Nagase, S.; Hanamura, M.; Morokuma, K. *J. Org. Chem.* **1984**, *49*, 631.

(45) For an early review on nucleophilic substitution, see: Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: New York, 1969.

(46) Schreiner, P. R. Dissertation, Universität Erlangen-Nürnberg, 1994.

(47) A referee's comment on the flatness of the potential energy surface is taken into consideration in the discussion of Table 3. For instance, the cation moiety in $TS_{exo}$, which is geometrically still at a considerable distance from the fully bridged ion, has almost the same energy as the nonclassical ion.

**Table 3. Comparisons of 2-Norbornyl Cation and Transition State Models at the B3LYP/6-311+G*//B3LYP/6-31G* Level[a]**

| row # | *exo* | ΔE (kcal mol$^{-1}$) | *endo* |
|---|---|---|---|
| 1 | expt. solvolysis TS energies with various leaving groups (OTs, OBs, OAc) | **4-6[5]** | expt. solvolysis TS energies with various leaving groups (OTs, OBs, OAc) |
| 2 | **TS$_{exo}$** | **3.7** | **TS$_{endo}$** |
| 3 |  , **3**, $C_s$<br>symmetrically bridged 2-norbornyl cation, minimum<br>0.0 | **13.1** |  , **5**, $C_1$<br>transition structure for rearrangement to the norpinyl cation<br>13.1 |
| 4 |  | **14.7** |  , - e$^-$, $C_1$<br>cation energy on radical geometry<br>14.7 |
| 5 | **TS$_{exo}$** without $H_2O$<br>(energy of **TS$_{exo}$** cation moiety)<br>1.3 | **7.5** | **TS$_{endo}$** without $H_2O$<br>(energy of **TS$_{endo}$** cation moiety)<br>8.8 |
| 6 | prot. 2-*exo*-norbornanol ground state without $H_2O$,<br>23.9 | **8.4** | prot. 2-*endo*-norbornanol ground state without $H_2O$,<br>32.3 |
| 7 | <br>cation with fixed norbornane geometry where *exo*- hydrogen at C2 was removed<br>40.7 | **8.1** | <br>cation with fixed norbornane geometry where *endo*- hydrogen at C2 was removed<br>48.8 |
| 8 | <br>radical with fixed norbornane geometry where *exo*- hydrogen at C2 was removed<br>6.5[b] | **2.0** | <br>radical with fixed norbornane geometry where *endo*- hydrogen at C2 was removed<br>8.5[b] |

[a] Relative energies vs the bridged 2-norbornyl cation minimum (**3**) are given below the structures; relative energy differences (Δ$E$) are given boldface in the center column. [b] Energy relative to optimized $C_1$ radical geometry.

the initial geometries further.[48] The computed activation energies for the model water leaving group system are, as expected, much smaller (*exo*, 2.8 kcal mol$^{-1}$, *endo*, 5.3 kcal mol$^{-1}$; Table 1)[42] than the experimentally found activation barriers for the solvolysis of 2-*exo*- and 2-*endo*-norbornyl tosylates (18−26 kcal mol$^{-1}$), since the latter involve the dissociation of neutral species where charge separation and ion solvation take place.

## Results and Discussion

**The Secondary 2-Norbornyl System (Figures 1 and 2).** The TS$_{exo}$ vs TS$_{endo}$ activation energy difference, Δ$E_a$, which *includes* the 1.2 kcal mol$^{-1}$ ground state energy difference, is 3.7 kcal mol$^{-1}$ (computed as 5.3 kcal mol$^{-1}$ −2.8 kcal mol$^{-1}$ + 1.2 kcal mol$^{-1}$) in favor of TS$_{exo}$ for the model solvolyses **1** (X = $OH_2^+$) → TS$_{exo}$ and **2** (X = $OH_2^+$) → TS$_{endo}$.[49] For water as the leaving group, Δ$E_a$ leads to a theoretical *exo*/*endo* ratio of 68 of the *exo* over the *endo* solvolysis rate at 298 K.

As these results are in general accord with experiment (Table 3, row 1), we can address the central question: Why is Δ$E_a$ much smaller than the *ca.* 14 kcal mol$^{-1}$ relative energy difference between the classical (**5**) and nonclassical (**3**) 2-norbornyl cations? Even though the C−O separations in TS$_{exo}$ (3.104 Å) and TS$_{endo}$ (2.396 Å) are quite large, the nonclassical nature of the *cation moieties* is not fully developed, even for TS$_{exo}$. This is apparent when the critical C1−C2, C1−C6, and C2−C6 distances in TS$_{exo}$ and TS$_{endo}$ are compared (Figure 1).

These results *appear* to support Winstein's[27] generalization that "bridging lags behind ionization" (*i.e.*, the nonclassical character is not fully developed for *exo* solvolysis), but only with regard to the degree of bridging.

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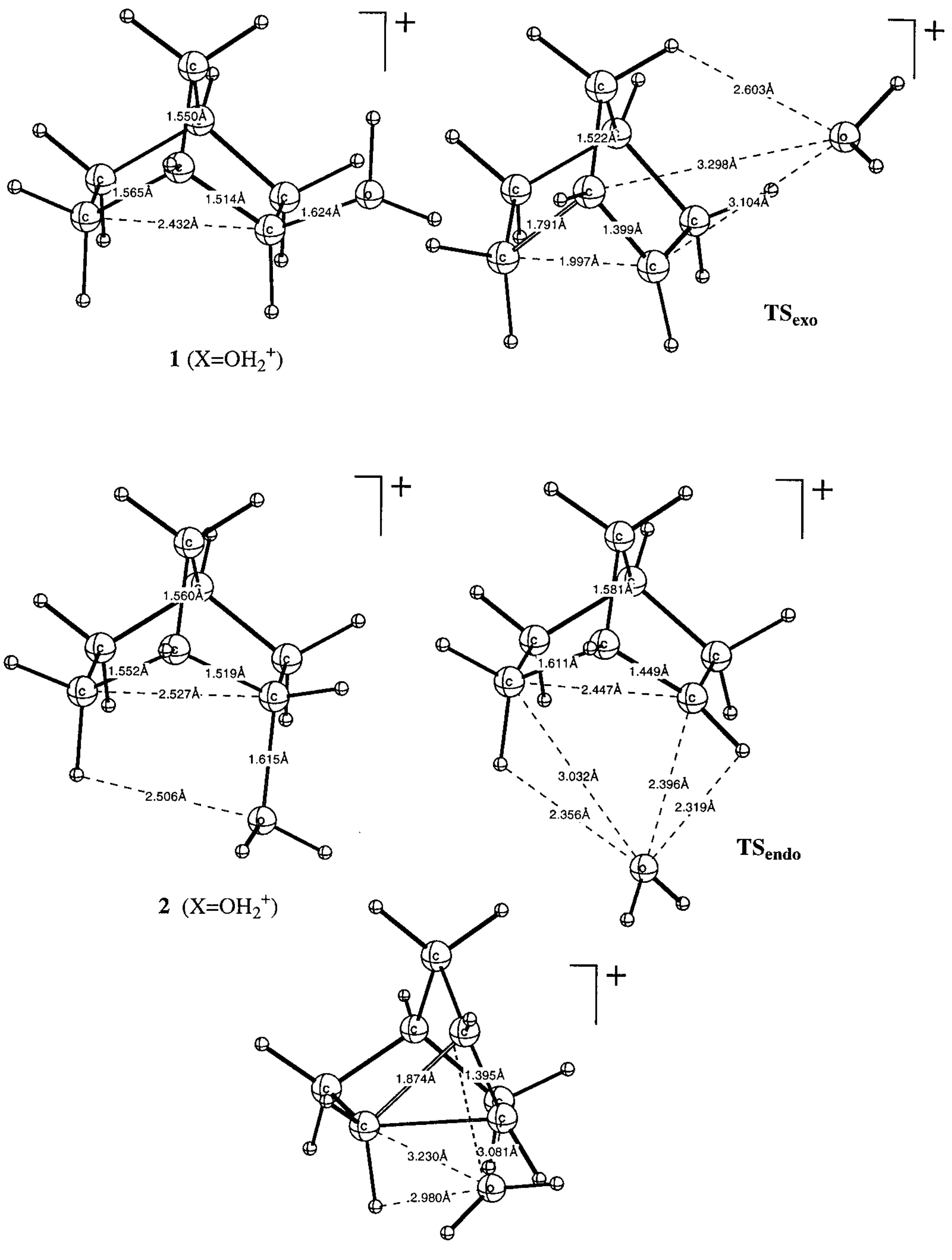
(48) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*; Gaussian Inc.: Pittsburgh, PA, 1993.

(49) The inclusion of entropy corrections (at 298 K: Δ$S$ in eu for **1** = 83.3, **2** = 83.1, TS$_{exo}$ = 93.0, TS$_{endo}$ = 87.6) favors *exo* solvolysis, to give ΔΔ$G_0^‡$ = 5.3 kcal mol$^{-1}$.



**1** ($X=OH_2^+$)

$TS_{exo}$

**2** ($X=OH_2^+$)

$TS_{endo}$

**6**

**Figure 1.** Ground and transition structures for the solvolysis of protonated *exo*- and *endo*-2-norbornanol at B3LYP/6-31G*.

However, the *energies* of the cation moieties of the transition states are more revealing than their geometries. To estimate how much both transition structures benefit from developing nonclassical character, we computed single-point energies (B3LYP/6-311+G*//B3LYP/6-31G*, Table 3) of $TS_{exo}$ and $TS_{endo}$ simply by removing the $H_2O$ leaving group and keeping the geometries of the cation moieties fixed (Table 3, row 5). The energies, relative to the fully bridged norbornyl cation minimum **3**, are remarkable: $TS_{endo}$(less $H_2O$) = 8.8 kcal $mol^{-1}$, $TS_{exo}$(less $H_2O$) = 1.3 kcal $mol^{-1}$! This demonstrates that *both cation moieties in their transition state geometries benefit from nonclassical stabilization relative to* **5**, *and both are delocalized*! Hence, Winstein's generalization only holds here for *structures* but not for *energies*! Although the bridging in $TS_{exo}$ is not fully developed geometrically, the energy of its cationic fragment is only slightly higher (1.3 kcal $mol^{-1}$) than that of the fully relaxed symmetrical 2-norbornyl cation (**3**).

How important is bridging in norbornyl systems? The energy comparisons of various *exo*- and *endo*-2-norbornyl cation models in Table 3 provide further insights. As stated above, the 2-norbornyl radical geometry also is a good model for the classical ion; the vertical ionization relative energy differs only by 1.6 kcal $mol^{-1}$ from that of **5** (*cf.* rows 3 and 4, Table 3).

The greater *exo* over *endo* stabilization of the cation moieties is near 8 kcal $mol^{-1}$ not only with the leaving groups deleted ($TS_{exo}$(less $H_2O$) and $TS_{exo}$(less $H_2O$), Table 3, row 5) but also in the ground states without $H_2O$ (Table 3, row 6). Computations in which a hydride ion in the 2-*exo*- and 2-*endo*-positions of norbornane, respectively, is deleted (not changing the hydrocarbon geometry otherwise) yield a similar *exo*−*endo* difference (8.1 kcal

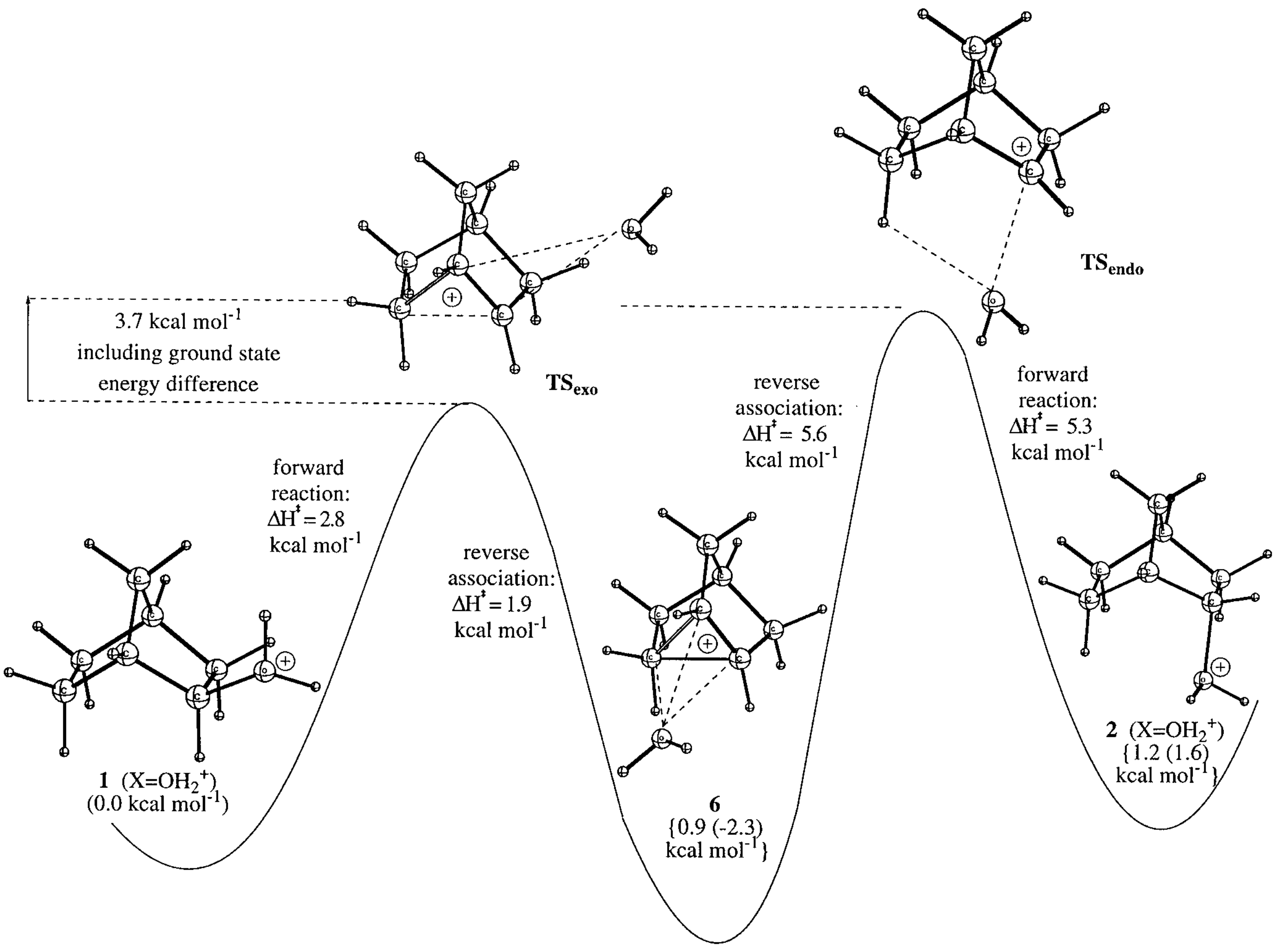


**Figure 2.** "Computational" Goering–Schewene diagram (not drawn to scale) at B3LYP/6-311+G*//B3LYP/6-31G*. The values in parentheses are the ZPVE-corrected energies for the ground states only. For a discussion, see also the Methods section and ref 42.

mol$^{-1}$, Table 3, row 7), although the energies relative to **3** and **5** are much higher. An *exo* preference is also found in the hypothetical, norbornane-based radicals (row 8), although less pronounced because of the smaller electron demand (vs the cation). *Thus, there is an energetic bias favoring exo over endo in the absence of any bridging.* This point was emphasized by H. C. Brown (see Introduction) and provides an explanation for the high *exo*/*endo* solvolysis rate ratios of tertiary norbornyl systems (Scheme 2). We stress that this differential effect already is apparent in the cation moieties of the protonated alcohol ground states (when the water molecules are deleted in the computations, row 6, Table 3) but is mostly electronic and not steric in origin. Hence, *bridging is not necessary for large exo over endo preferences.* Bridging is a consequence of the stabilization which is greatly enhanced in the nonclassical 2-norbornyl cation. Note the large change in the relative energies of the 2-*exo*-cation models, 40.7 (row 7), 23.9 (row 6), and 1.3 (row 5) kcal mol$^{-1}$.

If the energy difference of the cation moieties in the *exo*- and *endo*-transition structures is 7.5 kcal mol$^{-1}$ (Table 3, row 5), and their activation energy difference is 3.7 kcal mol$^{-1}$ (derived from the relative energies in Table 2, including the 1.2 kcal mol$^{-1}$ ground state energy difference), there must be remaining interactions which favor the *endo* transition structure by about 3.8 kcal mol$^{-1}$. What is the origin of this extra stabilization of the *endo*- over the *exo*-transition structure?

Differences in the degrees of interaction with the leaving groups in TS$_{exo}$ and TS$_{endo}$ are responsible! Although the C···O distances in the TSs are quite large, the interaction energies of the cation moieties with $H_2O$ are quite substantial (*exo* = 10.6 kcal mol$^{-1}$, *endo* = 11.3 kcal mol$^{-1}$, using the fixed cation geometries of the transition structures in the computation). Hence, this residual stabilization by the leaving group must *compete* with neighboring participation, particularly in the *exo* case. As a consequence of this competition between C1–C6 bond participation and the interaction with the leaving group, only part of the potential neighboring group driving force is realized in TS$_{exo}$.

The *endo* system behaves more normally. The C···O and the two closest H···O distances for TS$_{endo}$ (C···O, 2.396 Å; H···O, 2.356 and 2.319 Å) are much smaller than those for TS$_{exo}$ (C···O, 3.104 Å; H···O, 2.463 and 2.603 Å). Since the O···H distances are within the usual hydrogen-bonding range, TS$_{endo}$ is stabilized more through the interaction with the leaving group than is TS$_{exo}$. Although this stabilization may be attenuated in solution, the usual leaving groups (from neutral solvolysis substrates) are negatively charged and CH···X$^-$ hydrogen-bonding will be more important.[50]

Note that the *endo* leaving group interaction in TS$_{endo}$ also assists in orienting the developing p-orbital on C2 by forcing the C2–H bond to move downward toward the *endo* face. Such an effect is hardly present in TS$_{exo}$ due

**Table 4. Comparison of Driving Force via Rearrangement and Acceleration During Solvolysis of 1-Substituted 2-*exo*-Norbornyl Systems**

| system | driving force (kcal mol$^{-1}$) | acceleration (kcal mol$^{-1}$) |
|---|---|---|
| 2-*exo*-norbornyl | 13 | 5 |
| 1-methyl-2-*exo*-norbornyl | 24 | 7 |
| 1-phenyl-2-*exo*-norbornyl | 40 | 6 |

to the large separation of the cation moiety and the leaving group.

As a consequence and in contrast to Brown's suggestion (see Introduction), we find that there is a *stabilizing* (rather than a repulsive, steric) interaction with the *endo*-hydrogen in the 6-position in TS$_{endo}$ (Figure 1)! As the C$_6$H$_{endo}$–oxygen bond length becomes shorter (from 2.506 to 2.356 Å), the hydrogen-bonding type interaction of the oxygen atom is *increased* in the transition vs the ground state structure.

The ground state difference between **1** (X = OH$_2^+$) and **2** (X = OH$_2^+$) is 1.2 kcal mol$^{-1}$ (1.6 kcal mol$^{-1}$ including ZPVE: expt: 1–2 kcal mol$^{-1}$),[5] which contributes significantly to the differences in activation energies. Solvolysis of both **1** (X = OH$_2^+$) and **2** (X = OH$_2^+$), summarized as a Goering–Schewene diagram in Figure 2,[5] eventually leads to the symmetrically bridged nonclassical 2-norbornyl cation–water complex **6** (Figure 1; note the similarity between the geometries of the cation moiety in **6** and the bridged norbornyl cation **3**). The computed activation energies for the reverse steps (1.9 kcal mol$^{-1}$ (**6** → TS$_{exo}$) and 5.6 kcal mol$^{-1}$ (**6** → TS$_{endo}$)) are consistent with the formation of a high excess of *exo* products due to the stronger partial covalent interaction to water in TS$_{endo}$ vs TS$_{exo}$. This also explains why the polarimetric rate of 2-*exo*-substituted norbornanes exceeds the titrimetric rate by a substantial amount:[21] both the *exo* solvolysis and *exo* internal return reactions occur more rapidly than their *endo* counterparts and also more rapidly than the separation into discrete species.

**The 1-Methyl-2-norbornyl System (Figure 3).** The situation in the 1-methyl (and 1-phenyl, see below) derivatives is even clearer because the structural and energetic effects are much larger in magnitude. Carbocation-stabilizing substituents at C1 accelerate the *exo* solvolysis to a remarkably small extent (less than 10$^2$ for 1-methyl, see Tables 1 and 4).[51] The large driving forces available through rearrangement to the tertiary methyl- (Scheme 1) and phenyl-substituted cations are *not* reflected in the corresponding solvolysis rates.

We calculated the ground structures (**7** and **8**, Figure 3) and transition structures (TS$_{me\text{-}exo}$ and TS$_{me\text{-}endo}$, Figure 3) for the model solvolysis of protonated 1-methyl-2-*exo*- and 2-*endo*-norbornanol at B3LYP/6-311+G*//B3LYP/6-31G*. The activation barriers for the H$_2$O separation are only 0.2 (*exo*) and 5.1 (*endo*) kcal mol$^{-1}$. An important finding is that the highly exothermic rearrangement to the tertiary system does not occur during the optimization, even to the *exo*-transition state. The very low activation energy computed for TS$_{me\text{-}exo}$[42] is due to the use of an uncharged leaving group. The barrier is much higher for the experimental solvolysis, RX → R$^+$ + X$^-$, of neutral substrates due to the developing charge separation. The 1-phenyl TS$_{ph\text{-}exo}$ is higher in energy than TS$_{me\text{-}exo}$ but has similar characteristics.

The energies of TS$_{me\text{-}exo}$ and TS$_{me\text{-}endo}$ also reflect the experimental 1-methyl substituent influences well. Equation 2 shows that the computed 1-methyl effect on the *endo*-2-norbornyl solvolysis is quite small. The influence of a 1-methyl group in the 2-*exo* solvolysis (eq 3) is significant. The computed *exo*/*endo* rate ratios, based on the 3.6 kcal mol$^{-1}$ difference (eq 3 minus eq 2) in favor of *exo* solvolysis, corresponds to the *ca.* 10$^2$ rate acceleration observed experimentally.[27] As a consequence, the computed transition structures, although having model character, do appear to represent the situation in a meaningful way.

$$\mathbf{7} + \mathrm{TS}_{endo} \rightarrow \mathbf{1}\ (\mathrm{X} = \mathrm{OH_2}^+) + \mathrm{TS}_{me\text{-}endo},\ \Delta H = 0.4\ \mathrm{kcal\ mol^{-1}} \quad (2)$$

$$\mathbf{8} + \mathrm{TS}_{exo} \rightarrow \mathbf{2}\ (\mathrm{X} = \mathrm{OH_2}^+) + \mathrm{TS}_{me\text{-}exo},\ \Delta H = -3.2\ \mathrm{kcal\ mol^{-1}} \quad (3)$$

The 1-methyl ground and transition states can be analyzed in detail (Table 5), following the procedures for the parent 2-norbornyl system, by employing a number of fixed geometry computations for various cation entities (Table 3). Thus, if the 1-methyl-2-norbornyl geometry is kept intact, the 1-methyl-2-*exo*- and 1-methyl-2-*endo*-norbornyl cations computed simply by replacing the appropriate hydrogens by a positive charge show the usual *exo* energy bias (7.8 kcal mol$^{-1}$, Table 5, row 6). This *exo*/*endo* bias differs very little from the 8.1 kcal mol$^{-1}$ found similarly with the parent norbornyl system (Table 3, row 7). Hence, in the absence of any relaxation, the 1-methyl substituent has little differential *exo*/*endo* effect.

Next, single-point energies of the cation moieties taken from the ground states (**7** and **8**) and from the transition states (TS$_{me\text{-}exo}$ and TS$_{me\text{-}endo}$) were computed by keeping the geometries fixed and deleting the H$_2$O molecule. For **7** and **8** (Table 5, row 5), the C$_8$H$_{13}^+$ *exo*/*endo* energy difference (9.2 kcal mol$^{-1}$) is only 0.8 kcal mol$^{-1}$ higher than the corresponding norbornyl value (Table 3, row 6). Hence, although the structures of the carbocation moieties have relaxed significantly, there is still little change due to the 1-methyl substituent.

However, the *exo*/*endo* energy difference of the C$_8$H$_{13}^+$ moieties taken from the transition structures (both TS$_{me\text{-}exo}$ and TS$_{me\text{-}endo}$ less H$_2$O) is nearly 2 times as large (17.3 kcal mol$^{-1}$, Table 5, row 4). This much larger value than the experimental solvolysis transition state energy differences (6–7 kcal mol$^{-1}$, Table 5, row 1) demonstrates the leaving group interaction effect even more dramatically than in the parent 2-norbornyl system. The leaving group interaction stabilizes TS$_{me\text{-}endo}$ 10.6 kcal mol$^{-1}$ more than TS$_{me\text{-}exo}$ (Table 5, row 4 minus row 2)!

Both the geometry (discussed in detail below) and the energy of TS$_{me\text{-}exo}$ show a modest degree of advancement along the reaction coordinate toward the tertiary cation **4** (Scheme 2). The energy of the C$_8$H$_{13}^+$ cation moiety in TS$_{me\text{-}exo}$(less H$_2$O) relative to **4** is appreciable (7.7 kcal mol$^{-1}$) vs only 1.3 kcal mol$^{-1}$ for the corresponding parent 2-*exo*-norbornyl cation situation (Table 5, row 3).

The difference between the parent and the 1-methyl solvolysis behavior also reflects the degree of structural reorganization necessary to go from the ground state to

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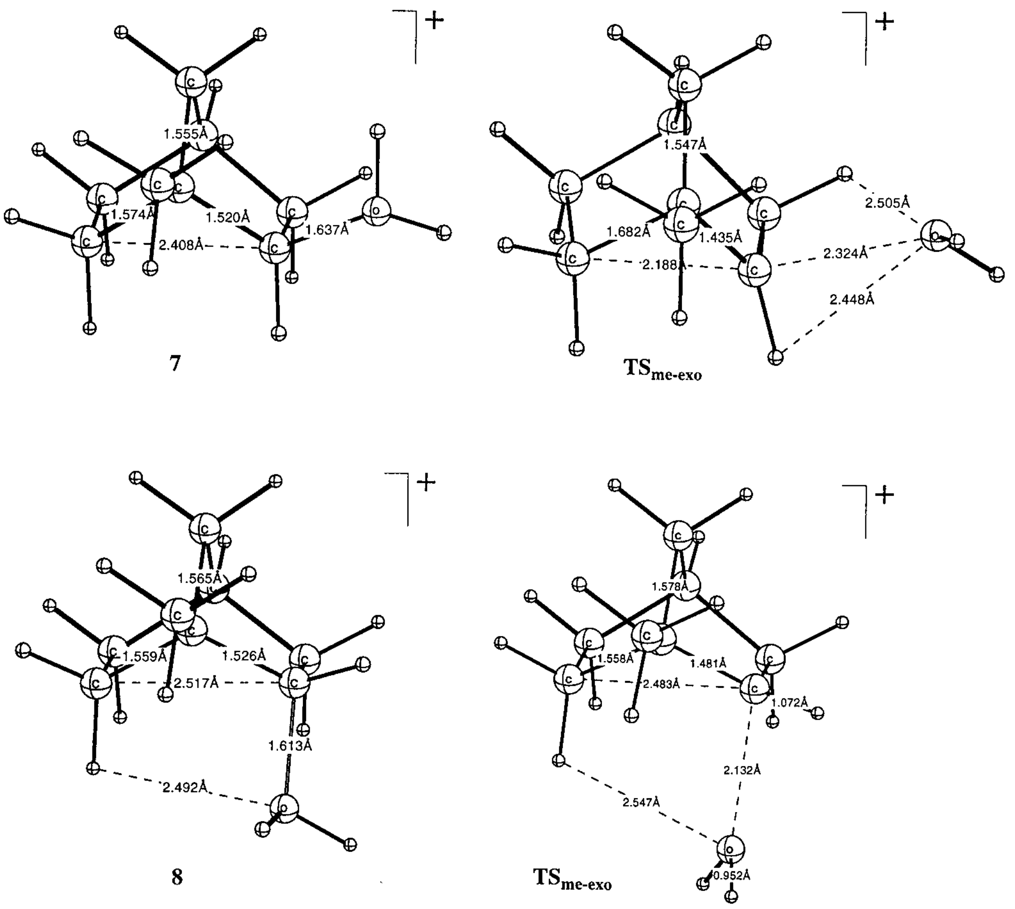
(50) The α-hydrogen bond complexation energies for [H$_2$CH–OH$_2$]$^+$, [H$_3$C–CH$_2$(bridged)–OH$_2$]$^+$, and [(CH$_3$)$_2$CH–OH$_2$]$^+$ are 19.8, 20.7, and 11.9 kcal mol$^{-1}$. For comparison (see also ref 19), the *exo* complexation energy for the classical 2-norbornyl cation (MP2/6-31G* geometry kept fixed) and water is 12.8 kcal mol$^{-1}$. Thus, **3** behaves like a typical secondary alkyl cation.

(51) Brown, H. C.; Rei, M.-H. *J. Am. Chem. Soc.* **1968**, *90*, 6216.



**7**

$TS_{me\text{-}exo}$

**8**

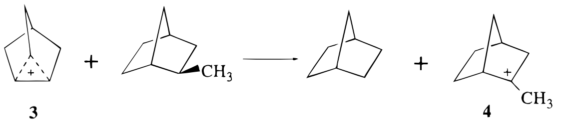
$TS_{me\text{-}exo}$

**Figure 3.** Ground and transition structures for the solvolysis of protonated 1-methyl-*exo*- and -*endo*-2-norbornanol at B3LYP/6-31G*.

the cation intermediate. For 2-*exo*-norbornyl only a relatively slight movement (principally of C6 and the attached atoms) is needed. However, in the 1-methyl-2-norbornyl system, C6 changes its primary attachment from C1 to C2. The entire skeleton must adjust to this bonding change, and this has not occurred to a very advanced extent in the transition structures, either $TS_{me\text{-}exo}$ or $TS_{me\text{-}endo}$.

*Bridging lags distinctly behind ionization **both** for structures* and for *energies* in $TS_{me\text{-}exo}$, in contrast to the unsubstituted 2-*exo*-norbornyl system. Hence, it is easy to understand why the cation moiety of $TS_{me\text{-}exo}$ benefits only to a small extent from stabilization of the developing charge at C1 by the 1-methyl group. The $TS_{me\text{-}exo}$(less $H_2O$) cation moiety is considerably higher in energy (7.7 kcal $mol^{-1}$, Table 5, row 4) than the free cation **4**. The corresponding 2-norbornyl $TS_{exo}$(less $H_2O$) value is only 1.3 kcal $mol^{-1}$ (Table 3, row 5). While the difference in stabilization of the cation fragments in $TS_{me\text{-}exo}$ and $TS_{me\text{-}endo}$ (both less $H_2O$) is much larger (9.8 kcal $mol^{-1}$, Table 5, row 4 minus row 5, Table 3) than those in the parent 2-norbornyl system, the corresponding ground state relative energy differences (1−2 kcal $mol^{-1}$, Table 2) are comparable.

Again, there is an attractive interaction in $TS_{me\text{-}endo}$ between the $C6_{endo}$−hydrogen and the leaving group, but this is diminished in $TS_{me\text{-}endo}$ vs $TS_{endo}$. The $C6_{endo}$−H···O distance *increases* in going to $TS_{me\text{-}endo}$ (it *decreases* in $TS_{endo}$, see above, Figure 1). Hence, the *exo* vs *endo* activation energy difference is larger for the 1-methyl than for the parent 2-norbornyl systems. The relatively small rate increase for *exo* solvolysis due to the 1-methyl substituent thus arises mainly from stabilization of the positive charge (when the hydrogen charge is summed into the carbon charge) on C1 for the parent *exo*- (charge on C1 in $TS_{exo}$: +0.289 e, NPA) and *endo*- (charge on C1 in $TS_{endo}$: +0.271 e, NPA) transition structures. The positive charge on C1 in the *exo*-transition structure is only marginally higher, and the stabilizing potential of the methyl group is ineffective. Hence, there is but little sensitivity to stabilizing substituents in the 1-position, and the 12.4 kcal $mol^{-1}$ (eq 4) greater stability of the “classical” (only partially bridged) 2-methyl-2-norbornyl cation (**4**) vs the nonclassical (symmetrically bridged) 2-norbornyl cation (**3**) is reflected to a greatly diminished extent in the activation energy difference of 6.8 kcal $mol^{-1}$.



3 4 (4)

ΔH = -12.4 kcal $mol^{-1}$ (B3LYP/6-31G*); $ΔH_f^o$ = -10.8 kcal $mol^{-1}$ (expt. ICR data)[52]

**The 1-Phenyl-2-norbornyl System (Figure 4).** Remarkably, despite the even greater potential driving force, a 1-phenyl substituent is *less* accelerating (by about 1 kcal $mol^{-1}$) than a 1-methyl substituent in 2-*exo*-norbornyl solvolysis (Table 1). The large $\pi$-stabilizing propensity of phenyl is *not* effective. Such retardations due to remote phenyl substituents have been observed

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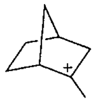
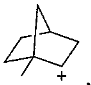
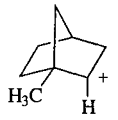
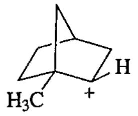
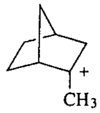
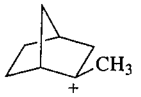
(52) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, (Suppl. 1), 1.

**Table 5. Influence of a Methyl Substituent on Cation Energies at B3LYP/6-311+G*//B3LYP/6-31G***

| row # | *exo* | ΔE (kcal mol$^{-1}$) | *endo* |
|---|---|---|---|
| 1 | expt. solvolysis TS energies with various leaving groups (OTs, OBs, OAc) | **6-7**[5] | expt. solvolysis TS energies with various leaving groups (OTs, OBs, OAc) |
| 2 | **$TS_{me-exo}$** | **6.7** | **$TS_{me-endo}$** |
| 3 | , **4**, $C_1$<br>2-methyl-2-norbornyl cation, minimum[a]<br>0.0 | **23.8** | , $C_1$<br>classical cation on radical geometry (vertical ionization)[a]<br>23.8 |
| 4 | **$TS_{me-exo}$** cation moiety without $H_2O$<br>7.7 | **17.3** | **$TS_{me-endo}$** cation moiety without $H_2O$<br>25.0 |
| 5 | ground state (**7**) cation moiety without $H_2O$<br>34.2 | **9.2** | ground state (**8**) cation moiety without $H_2O$<br>43.4 |
| 6 |  <br>cation fixed 1-methyl norborane geometry where *exo*-hydrogen at $C_2$ was removed<br>49.0 | **7.8** |  <br>cation fixed 1-methyl norborane geometry where *endo*-hydrogen at $C_2$ was removed<br>56.8 |
| 7 |  <br>cation fixed 2-*endo*-methyl norborane geometry where *exo*-hydrogen at $C_2$ was removed<br>37.5 | **6.1** |  <br>cation fixed 2-*exo*-methyl norborane geometry where *endo*-hydrogen at $C_2$ was removed<br>43.6 |

[a] Note that the ionization potentials (IP) for the 2-norbornyl and 1-methyl-2-norbornyl radicals are comparable (160.9 and 163.0 kcal mol$^{-1}$, respectively). The IP for the 2-methyl-2-norbornyl radical is smaller (142.9 kcal mol$^{-1}$).

in related participating systems (see Introduction) and are attributed to the electron-withdrawing inductive effect of phenyl.[53] There is a complicating feature, $\pi\cdots H-O$ bonding, which is not present in the alkyl derivatives. This interaction is greater in the computed *endo* than *exo* ground and transition states and influences the relative energies of both significantly. Such $\pi\cdots H-O$ interactions would, of course, be unimportant in actual solvolysis involving anionic leaving groups.

Our computations even yield a higher barrier for the *exo*/*endo* difference for the 1-phenyl-substituted system ($\Delta E_a(TS_{ph-exo})$ = 4.0 kcal mol$^{-1}$, $\Delta E_a(TS_{ph-endo})$ = 8.9 kcal mol$^{-1}$; Table 2) compared to the parent case. The larger ground state relative energy difference (4.2 kcal mol$^{-1}$, **9** vs **10**) than the unsubstituted and 1-methyl-substituted cases (1−2 kcal mol$^{-1}$) can be attributed to the $\pi\cdots H-O$ hydrogen-bonding stabilization in **9**.[54] However, our main concern is with the *exo* and *endo* transition states, $TS_{ph-exo}$ and $TS_{ph-endo}$.

Judged against the available driving force of about 40 kcal mol$^{-1}$ (Table 4), the experimental 1-phenyl-2-*exo*-norbornyl solvolysis is very weakly accelerated. Although the phenyl ring adopts a perpendicular orientation (relative to the C1−C2−C6 norbornyl fragment plane) in $TS_{ph-exo}$ which should be *favorable* for interaction with the developing "vacancy" in the C1−C6 bond, *the norbornyl cation fragment in* $TS_{ph-exo}$ *exhibits less bridging than in* $TS_{exo}$! The C1−C6 bond length (1.740 vs 1.791 Å) is shorter, and the C1−C2 bond is longer (1.425 vs 1.399 Å, in $TS_{ph-exo}$ vs $TS_{exo}$, respectively). As with $TS_{exo}$, the residual interaction with the leaving group in $TS_{ph-exo}$ competes effectively with participation. The destabilizing inductive effect of phenyl (vs H or $CH_3$)[53] actually dominates over the benzyl cation-stabilizing potential.

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(53) (a) Schleyer, P. v. R.; Woodworth, C. W. *J. Am. Chem. Soc.* **1968**, *90*, 6528. (b) Lancelot, C. J.; Harper, J. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 4294. (c) Apeloig, Y.; Arad, D.; Lenoir, D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1981**, *22*, 879. (d) Lenoir, D.; Apeloig, Y.; Arad, D.; Schleyer, P. v. R. *J. Org. Chem.* **1988**, *53*, 661.

(54) Schleyer, P. v. R.; Trifan, D. S.; Bacskai, R. *J. Am. Chem. Soc.* **1958**, *80*, 6691.

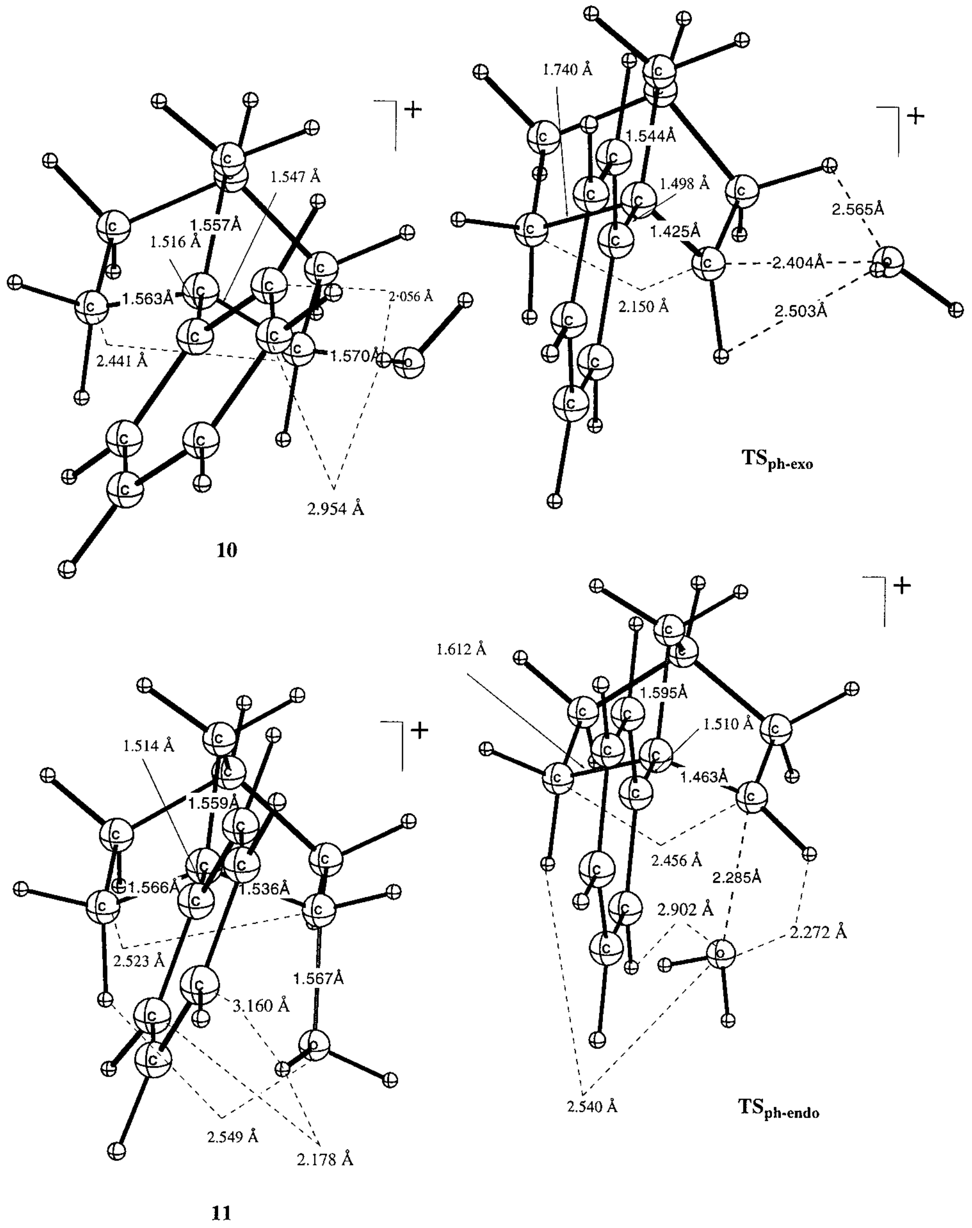

**Figure 4.** Ground and transition structures for the solvolysis of protonated 1-phenyl-*exo*- and -*endo*-2-norbornanol at B3LYP/6-31G*.

Bridging is much less pronounced in $TS_{ph\text{-}endo}$ than in the parent case ($TS_{endo}$), and the 1-phenyl group-stabilizing potential is not utilized. As was found for $TS_{me\text{-}endo}$, the CH···O hydrogen-bonding interaction in $TS_{ph\text{-}endo}$ between the leaving group and the *endo*-hydrogen at C6 is diminished vs $TS_{endo}$ (the O···H distance is longer by 0.184 Å in $TS_{ph\text{-}endo}$). As this is generally a significant stabilizing contribution for *endo* dissociation, the 1-phenyl activation barrier (*i.e.*, $TS_{ph\text{-}endo}$, $E_a = 8.9$ kcal mol$^{-1}$) is even higher than that for the parent *endo*-norbornyl system (*i.e.*, $TS_{endo}$, $E_a = 5.3$ kcal mol$^{-1}$).

## Conclusions

We have analyzed in detail why only a fraction of the computed 13−14 kcal mol$^{-1}$ energy difference between the nonclassical (**3**) and the classical (**5**) 2-norbornyl cations is reflected in the experimental *exo* vs *endo* solvolysis transition state activation energy differences (4−6 kcal mol$^{-1}$). Furthermore, the discrepancy between the large additional driving forces available to cation-stabilizing 1-methyl and 1-phenyl substituents and the actual solvolysis data (rate accelerations of only $10^2$ or less) also is explained by differential interactions of the leaving group with the cations in the transition states.

In our model study, water was used as a neutral leaving group to insure the heterolytic bond cleavage at the 2-position. The computed transition states also model the reverse reactions, the nucleophilic attack of the intermediate by water. The computed differences in activation energies (3.7 kcal mol$^{-1}$) for loss of a $H_2O$ molecule (vis $TS_{exo}$ and $TS_{endo}$) from protonated 2-*exo*- and 2-*endo*-norbornyl alcohols agree well with experimental solvolysis activation barrier differences (4−6 kcal mol$^{-1}$). Thus, such neutral leaving group models are effective for the study of heterolytic bond dissociation and association processes computationally.

We dissected the transition state energy differences in a very direct way. Taking, *e.g.*, the $TS_{exo}$ and $TS_{endo}$ geometries, we computed the single-point energies of the cation moieties remaining after simply deleting the $H_2O$

molecules. The data provide an energy difference for the cation moieties in the transition structures, *exo* and *endo*, themselves as well as comparisons with the energy of the fully relaxed 2-norbornyl cation. Furthermore, the energy difference for interaction of the water molecules in the *exo*- and *endo*-transition states is obtained by subtraction. That compensating effects are operating is demonstrated clearly: while the *cation moiety* in $TS_{exo}$-(less $H_2O$) is stabilized by 7.5 kcal mol$^{-1}$ over $TS_{endo}$(less $H_2O$), interaction with the $H_2O$ leaving group favors $TS_{endo}$ by 3.7 kcal mol$^{-1}$ over $TS_{exo}$; hence, the net difference between $TS_{exo}$ and $TS_{endo}$ is only 3.8 kcal mol$^{-1}$.

The 1-methyl-2-norbornyl behavior is even more dramatic. Although the intermediate is the rearranged and much more stable tertiary 2-methyl-2-norbornyl cation (**4**), the large driving force is only weakly reflected by the $10^2$ 1-methyl-2-*exo*-norbornyl rate acceleration. Here, the model computations find $TS_{me\text{-}exo}$ to be 6.8 kcal mol$^{-1}$ more stable than $TS_{me\text{-}endo}$. However, the quite large difference in the cation moieties (17.3 kcal mol$^{-1}$, $TS_{me\text{-}exo}$(less $H_2O$) vs $TS_{me\text{-}endo}$(less $H_2O$)) is counterbalanced by a 10.6 kcal mol$^{-1}$ solvation energy difference favoring the *endo*-transition structure. Competition between the stabilizations due to bridging and leaving group interactions is even greater in the 1-methyl than unsubstituted 2-norbornyl systems.

As far as *geometries* are concerned, Winstein's hypothesis that "bridging lags behind ionization" has some validity, but the degree depends on the system and the full interpretation is more complex. Although $TS_{exo}$ is not fully bridged, the energy of its cation moiety computed by omitting the leaving group ($TS_{exo}$(less $H_2O$)) is only 1.3 kcal mol$^{-1}$ higher than that of the fully bridged free norbornyl cation (**3**). Consequently, the *energy* of the *exo*-$C_7H_{11}^+$ moiety does *not* "lag behind". Incomplete bridging is thus *not* the full explanation for the difference between *exo*/*endo* solvolysis activation barriers and the *ca*. 14 kcal mol$^{-1}$ energy difference of the classical vs the nonclassical 2-norbornyl cations.

A strong *exo* bias is apparent in restricted norbornyl cation geometry models: bridging is *not* necessary for the large *exo*/*endo* preferences but enhances the effect. Hence, the tertiary 2-methyl and 2-phenyl solvolyses, which give tertiary ion intermediates in which bridging is less developed, also exhibit large *exo*/*endo* ratios. These tertiary ratios are smaller than in the secondary systems because of the compensating interaction with the leaving group which favors the (secondary) *endo*- over the *exo*-transition state.

In contrast to Brown's "repulsion" argument, there is a *stabilizing* interaction between the *endo*-hydrogen at C6 and the leaving group in the 2-*endo*-norbornyl TS. Similar bonding interactions to hydrogen are less effective in the *exo*-TS, where there is *competition* for cation stabilization between the leaving group and the hyperconjugating C1−C6 bond. This competition—larger in the 2-*exo*-systems—is responsible for reducing the *exo*/*endo* solvolysis activation energy ratios from the much greater values expected from the large relative energy difference between the bridged and the classical 2-norbornyl cations.

In 1-methyl- and 1-phenyl-2-norbornyl systems, bridging *does* lag behind ionization, both *structurally* and *energetically*. Due to incomplete bridging, the 1-substituents contribute minimally to transition structure stabilization. Residual interactions with the leaving group in the *exo*-TSs dominate and are responsible for the once puzzling behavior.

**Acknowledgment.** This research was supported by the Fonds der Chemischen Industrie, the Convex Computer Corp., the Stiftung Volkswagenwerk, and the U.S. Department of Energy (Office of Basic Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant DE-FG09-87ER13811). We thank D. Lenoir for helpful discussions. P.R.S. acknowledges Nicolaas van Eikema Hommes for technical assistance in the optimization of the very large 1-phenylnorbornyl systems. The Gaussian 94 optimization of the 1-phenyl-2-*exo*-transition structure took 350 CPU hours on a Convex SPP parallel computer with 32 HP735 processors (equivalent to 1.3 years on a single processor!).

**Supporting Information Available:** Cartesian coordinates for all computed structures at B3LYP/6-31G* (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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