Table X. Appendix: Force-Field Parameters and Nonbonded Interactions

Force-Field Parameters Used

bond	k_b	r_b, Å
C–C	300	1.525
C–O	300	1.430

angle	k_a	θ_a, deg
O–C–C	46.5	112
C–O–C	46.5	111

dihedral	$k_{d,2}$	$k_{d,3}$	γ
O–C–C–O	1.0	3.0	0
C–C–O–C		1.0	0

Nonbonded Interactions

atom	α	N_{eff}	R_i^0
C	1.77	7.0	1.90
O	0.64	7.0	1.6
Na^+	0.24	10.0	1.6
K^+	1.23	18.5	2.0
Rb^+	1.90	22.0	2.2
Cs^+	4.26	30.0	2.4

[a] Units are kcal/Å^2/mol for k_b, kcal/radian^2/mol for k_a, kcal/mol for $k_{d,n}$. The relation between the polarizability, α, the effective atomic number, N_{eff}, the ionic radius, R_i^0, and the parameters A and B is given in reference 38.

be particularly valuable in the design of synthetic receptors which can recognize guest species with high specificity.[2,55]

Acknowledgment. Peter A. Kollman would like to acknowledge the support of the N.I.H. (CA-25644 and GM-29072) in this research. G.W. has been supported by the N.S.F. in the form of a US–French Binational Fellowship and by a NATO grant. The UCSF Computer Graphics Lab, Robert Langridge, Director, supported by N.I.H. RR-1081-03, has been essential to all phases of this study. We thank U. Burkert for his comments on the manuscript and Andrew Dearing for the use of his modeling program CHEM.

Registry No. 18-crown-6, 17455-13-9; Na^+ 18-crown-6, 31270-12-9; K^+ 18-crown-6, 31270-13-0; Rb^+ 18-crown-6, 51390-80-8; Cs^+ 18-crown-6, 31270-14-1; Na^+ 18-crown-6$(OH_2)_2$, 81388-94-5; K^+ 18-crown-6$(OH_2)_2$, 69718-27-0; Rb^+ 18-crown-6$(OH_2)_2$, 81388-93-4; Cs^+ 18-crown-6$(OH)_2$, 81388-92-3; pentaglyme, 1191-87-3; Na^+ pentaglyme, 12562-88-8; K^+ pentaglyme, 12562-86-6; Rb^+ pentaglyme, 81388-91-2; Cs^+ pentaglyme, 81388-90-1; Na^+OH_2, 36606-66-3; K^+OH_2, 38682-53-0; Rb^+OH_2, 38682-54-1; Cs^+OH_2, 38682-55-2; $Na^+(OH_2)_6$, 40791-39-7; $K^+(OH_2)_6$, 40791-40-0; $Rb^+(OH_2)6$, 81020-89-5; $Cs^+(OH_2)6$, 81009-34-9; Na, 7440-23-5; K, 7440-09-7; Rb, 7440-17-7; Cs, 7440-46-2; $O(CH_3)_2$, 115-10-6; OH_2, 7732-18-5.

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Complete Theoretical Structures for the Classical and Nonclassical Forms of the 2-Norbornyl Cation and for Edge-Protonated Nortricyclene

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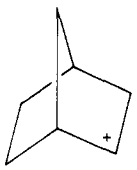
Abstract: Fully optimized geometries for the classical and nonclassical structures of the 2-norbornyl cation and for an edge-protonated nortricyclene have been determined with use of a split valence 4-21G basis set and a gradient procedure. At these optimized geometries the relative SCF energies in kcal/mol were as follows: classical structure 0.0, nonclassical structure +0.2, and edge-protonated nortricyclene +17.3. Additional calculations at these geometries with a standard C(9s5p/4s2p), H(4s/2s) double-ζ basis set yielded the following energy differences: classical form (0.0), nonclassical form (+1.0), and edge protonated nortricyclene (+17.8). The 4-21G basis set augmented by sets of d polarization functions on *all seven carbons* predicted the relative SCF energies: classical (0.0), nonclassical (−0.2), and edge protonated (+12.4). Thus, the classical and nonclassical forms are essentially equal (within tenths of a kcal/mol) in energy at these levels of theory. However, if one is justified in assuming that the effects of electron correlation will be analogous to what is found for smaller carbonium ions, then the nonclassical norbornyl cation will ultimately prove to lie lower in energy. The classical structure is predicted to be closer in geometry to the nonclassical one than was found in previous work. The geometry suggests that the classical isomer might best be viewed as an unsymmetrically bridged species.

One of the longest lasting controversies in physical organic chemistry has been concerned with the structure of the cation formed from the solvolysis of *exo*-2-norbornyl derivatives.[2a] A vast amount of experimental effort over the past 30 years has attempted to clearly establish whether the classical norbornyl cation **1** or the nonclassical structure **2** is more stable (or exists?) and whether one or the other form can best rationalize the considerable experimental data. More recently, new techniques[2b] such as carbon-13 NMR and X-ray photoelectron spectroscopy have been brought to bear on this problem. The orthodox view that the norbornyl cation has a nonclassical structure has recently been succinctly but forcefully restated by Schleyer and Chandrasekhar.[3] They conclude that the secondary 2-norbornyl cation has an extra stabilization of 6 ± 1 kcal/mol in stable ion media. Although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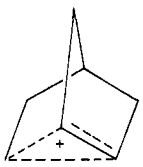
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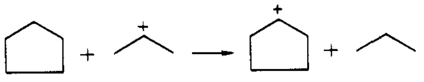
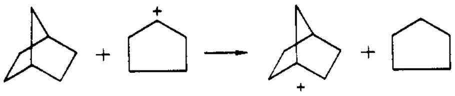
this stabilization might be due to effects other than bridging, these authors quote the latest direct spectroscopic observations[4-7] on the 2-norbornyl cation in nonnucleophilic media. The ESCA spectrum has been redetermined[4,5] and interpreted in terms of a nonclassical ion. An analysis[6] of the ^{13}C NMR chemical shifts of the 2-norbornyl cation would appear to demonstrate its bridged nature. Particularly noteworthy are the experiments by Saunders and Kates[7] using the deuterium isotopic perturbation probe technique. The absence of a large splitting in the ^{13}C NMR resonances is not consistent with a rapid rearrangement of classical ions but is compatible with a static, symmetrical structure. Arnett and co-workers[8] have recently presented evidence that the 2-norbornyl ion enjoys special thermodynamic stability (by as much as 7.5 kcal/mol) relative to other simple secondary carbonium ions in SO_2ClF/SbF_5 solvent. Gas-phase studies[9-12] to which the theoretical results of this work speak most directly have also indicated a special stability for the 2-norbornyl cation relative to other secondary ions. Saluja and Kebarle[12] have measured proton transfer equilibria and their temperature dependence with a high-pressure mass spectrometer. The two heats of greatest interest were



(1)

$\Delta H = -5.9$ kcal/mol

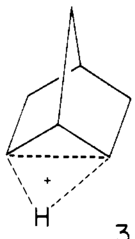


(2)

$\Delta H = -11.4$ kcal/mol

If the stabilization in reaction 1 is assumed to be due to "usual" factors, then the ΔH of reaction 2 indicates that some 6 kcal/mol additional exothermicity must be assigned to "special factors due to the specific structure of norbornyl cation".[12] The connection of the gas-phase results to solving the classical–nonclassical norbornyl ion controversy which chiefly concerns solvolysis reactions[2a] has been summarized by Kebarle.[12] To relate the gas-phase results to those in solution, we must consider the energy change due to differential solvation of the cations. It has been suggested by Jorgensen[13] on the basis of MINDO/3 calculations that the more charge-delocalized nonclassical ion will be less well solvated by the nucleophilic solvents commonly used. The "classical" position, which requires a small energy difference between the two structures in solution, then requires an even smaller energy difference in the gas phase if these arguments regarding solvation hold. The "nonclassical" position requires the gas-phase energy of the nonclassical ion to be lower.

As has been pointed out by Dewar,[14] theoretical calculations should be of especial value in helping to settle the question of the relative stabilities of the various forms of the 2-norbornyl cation. However, such calculations must meet some strict criteria to be judged reliable. In ab initio work, a basis set of double-ζ quality represents a minimum standard. Only the most fully tested and reliable semiempirical methods (such as MINDO/3) should be considered. Full geometry optimization with a gradient procedure is necessary in either approach.



3

A number of theoretical studies[14-18] of the various structures of the 2-norbornyl cation have appeared which meet *some* of the above-mentioned criteria. MINDO/3 calculations[14] with full geometry optimization predicted the classical ion to be 1.9 kcal/mol more stable than the nonclassical structure. However, the nonclassical structure was not a stable species according to the MINDO/3 results but rather a symmetrical transition state for the degenerate rearrangement of two classical structures. An edge-protonated nortricyclene **3**, was found to lie only 2.8 kcal/mol higher than the classical 2-norbornyl cation. Although the authors[14] urge caution due to the small energy differences relative to the inherent accuracy of MINDO/3 calculations, they suggest that the ion is likely to have the classical structure.

Goetz, Schlegel, and Allen[15] employed both minimal STO-3G and split-valence 4-31G basis sets in calculations on the classical and nonclassical structures. Partial geometry optimizations were carried out by a cyclic variation of key geometrical parameters and the procedure calibrated by gradient calculations. At the STO-3G level, the nonclassical ion was 5.2 kcal/mol higher in energy than the classical conformation, while with the 4-31G basis the difference was 0.2 kcal/mol. These authors argue on the basis of calculations on the much smaller ethyl and vinyl carbocations,[19] which included d functions on C and p functions on H, that the nonclassical form should be differentially stabilized by 4–8 kcal/mol upon the addition of polarization functions. In addition, in the ethyl cation[20] correlation effects favor the nonclassical form by 8 kcal/mol, and these authors suggest a similar value for $C_7H_{11}^+$. Thus, in the gas phase, the nonclassical 2-norbornyl cation is predicted to be more stable after approximate corrections for basis-set extension and correlation effects. Certain structural features determined by these ab initio calculations differed significantly from the MINDO/3 results. Clark, Cromarty, and Colling[16] used these optimized geometries to calculate the core hole X-ray ionization spectra with a split-valence basis set.

Wenke and Lenoir[17] combined MINDO/3 geometry optimizations with minimal basis set (STO-3G) ab initio calculations. The nonclassical ion was predicted to be 5.9 kcal/mol higher in energy than the classical form when STO-3G at the MINDO/3 geometries was used. Köhler and Lischka[18] employed a double-ζ contraction of a C(7s3p) and H(3s) basis set. In addition, d functions were included on *certain* of the carbon atoms in the molecule. Geometries were taken either from MINDO/3 or from STO-3G calculations. Valence shell electron correlation effects were estimated by a CEPA-PNO scheme with interpair interactions between nonneighbor localized bonds computed by the IEPA scheme. The classical form was predicted to be 0.8 kcal/mol more stable than the nonclassical conformer at the SCF level. Inclusion of d functions on *certain* of the carbons near the position of the formal positive charge preferentially stabilized the nonclassical ion (by ~3 kcal/mol), yielding an energy ~2 kcal/mol lower than the classical one. CEPA/IEPA correlation energy calculations further stabilized the nonclassical cation, placing it

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Table I. Total Energies (hartrees) and Relative Energies (kcal/mol) of the 2-Norbornyl Cation Isomers[a]

	total energies			relative energies		
cation	4-21G	DZ	4-21G+d	4-21G	DZ	4-21G+d
2-norbornyl, classical	−270.66633	−271.10869	−270.79047	0.0	0.0	0.0
2-norbornyl, nonclassical	−270.66598	−271.10710	−270.79085	0.2	1.0	−0.2
edge-protonated nortricyclene	−270.63880	−271.08037	−270.77066	17.3	17.8	12.4

[a] All calculations were performed at the optimized 4-21G geometries.

a full 13 kcal/mol lower in energy than the classical structure. Kohler and Lischka[18] stressed the possible importance of edge-protonated nortricyclene in the interpretation of gas-phase results on $C_7H_{11}^+$. At the SCF level, this edge-protonated form was predicted to be 17.4 kcal/mol less stable than the classical 2-norbornyl cation. Inclusion of d functions on certain carbons decreased the difference by ~10 kcal/mol to 7 kcal/mol, and the estimated correlation effects from CEPA/IEPA calculations were sufficiently large to place edge-protonated nortricylene 8 kcal/mol lower in energy than the classical ion. However, IEPA or approximate CEPA procedures have been criticized as yielding too much stabilization of the nonclassical forms in the case of the vinyl cation[35] and of $C_3H_7^+$.[36]

In the present work a near-double-ζ basis set has been employed in a *full*, rigorous geometry optimization using gradient methods. The effect of polarization functions has been examined on $C_7H_{11}^+$ itself by adding d functions to *all* carbons in these ions.

Theoretical Methods

Optimized geometries were determined for the classical, nonclassical, and edge-protonated structures starting from initial structural values derived from previously published work.[14,15] All optimizations were performed with a 4-21G split-valence basis set,[21] which has been shown to be of comparable quality to the more frequently employed 4-31G basis set.[22] Analytic gradients were calculated[23,24] at all points in the optimization and used in conjunction with a least-squares minimization of the gradient norm to predict the next geometry. The integral, SCF, and gradient program package developed by Pulay[24] was used for most of the calculations. All internal coordinate forces were less than 3.5×10^{-3} mdyn in magnitude for the final geometries.

The nonclassical and edge-protonated structures were optimized with retention of a plane of symmetry (see Figures 2 and 3). The final geometries were slightly distorted (by breaking this symmetry constraint) toward the classical geometry to provide a partial check that they represented minimum energy forms.

At the 4-21G optimized geometries additional SCF calculations were carried out with the standard Huzinaga–Dunning[25,26] double-ζ basis. These calculations allow an assessment of basis-set extension effects, i.e., the sp saturation of the basis on the relative energies of the three species. More importantly, the effects of polarization functions on the relative energies of the three ions were explicitly examined by calculations with the 4-21G basis set augmented by sets of six Cartesian Gaussian d functions with exponent 0.75 on *all seven* Carbons.

Most of the computations were carried out on the CYBER 175/750 computers of the University of Texas Computation Center. The 4-21G+d calculations were performed at the Institute for Molecular Science, Okazaki, Japan.

Results and Discussion

Energies. The total and relative energies of the 2-norbornyl cations at three levels of SCF theory are presented in Table I. All results are reported for the 4-21G optimized geometries. The 4-21G relative SCF energies of the classical ion, 0.0, nonclassical isomer, +0.2, and edge-protonated nortricyclene, +17.3 kcal/mol, are comparable to the results of Köhler and Lischka[18] (classical 0.0, nonclassical +0.8, edge protonated +17.4 kcal/mol), who employed a (7s3p/3s) basis set contracted to double-ζ but used STO-3G optimized geometries. The 4-21G energy difference between the classical and nonclassical forms of 0.2 kcal/mol agrees with the 4-31G result of Goetz, Schlegel, and Allen[15] for this quantity at less completely optimized geometries. Within the 4-21G SCF model, it may be concluded that the classical and nonclassical isomers of the 2-norbornyl cation are nearly isoenergetic while edge-protonated nortricyclene is definitely less stable.

The results with the standard C(9s5p/4s2p), H (4s/2s) double-ζ basis set[25,26] at the 4-21G geometries serve to illustrate that for hydrocarbons the 4-21G split-valence basis set is essentially of double-ζ quality in terms of the predictions of relative energy. The DZ SCF energy ordering is as follows: classical, 0.0; nonclassical, +1.0; and edge-protonated nortricyclene, +17.8 kcal/mol. The larger sp basis set causes very slight changes in the relative stabilities of the three cations. The total energies with the double-ζ basis are, of course, considerably lower (by more than 0.4 hartree) than the 4-21G ones.

The relative SCF energies with the 4-21G+d basis set at the 4-21G optimized geometries are as follows: classical 0.0, nonclassical −0.2, and edge-protonated nortricyclene at 12.4 kcal/mol. Thus compared to the 4-21G results, edge-protonated nortricyclene is preferentially stabilized by 4.9 kcal/mol due to the addition of d functions to the basis set. The classical and nonclassical ions remained close in energy, but the nonclassical norbornyl cation is now very slightly lower (0.2 kcal/mol) in energy. The preferential stabilization of edge-protonated nortricyclene by d functions could be anticipated from the results of Köhler and Lischka[18] using d functions on only selected carbon atoms and STO-3G optimized geometries. However, the differential stabilization of edge-protonated nortricyclene in this work (4.9 kcal/mol) is considerably less than that (~10 kcal/mol) found by Köhler and Lishka.[18] Interestingly, the present results do *not* show a strong stabilization of the nonclassical 2-norbornyl cation relative to the classical cation upon the inclusion of d functions in the basis set. The nonclassical form is stabilized by only 1.2 kcal/mol. The greater structural similarity of the classical and nonclassical norbornyl cations as revealed in the 4-21G optimized geometries of this study (vide infra) compared to earlier work probably accounts for the lack of differential stabilization due to d functions. In addition, very recent calculations on $C_3H_7^+$ isomers[36,37] have indicated that polarization functions alone gave little change in the relative energies of the 2-propyl cation (analogous to the classical 2-norbornyl cation) and corner-protonated cyclopropane (comparable to the nonclassical $C_7H_{11}^+$ system) while

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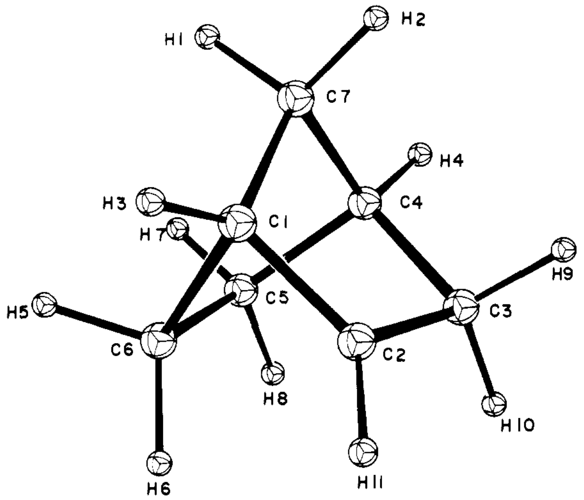

Figure 1. Fully optimized 4-21G geometry of the classical 2-norbornyl cation. Bond lengths (Å): C1–C2, 1.406; C1–C6, 1.753; C1–C7, 1.539; C6–C5, 1.543; C2–C3, 1.501; C5–C4, 1.547; C3–C4, 1.556; C4–C7 1.547; C7–H1, 1.079; C7–H2, 1.082; C1–H3, 1.071; C4–H4, 1.075; C5–H7, 1.080; C5–H8, 1.080; C6–H5, 1.080; C6–H6, 1.081; C3–H9, 1.090; C3–H10, 1.079; C2–H11, 1.074; C2–C6, 2.129. Bond angles (deg): C1–C7–C4, 96.9; C7–C4–C3, 101.4; C7–C4–C5, 102.4; C5–C4–C3, 105.4; C7–C1–C2, 107.3; C7–C1–C6, 99.1; C6–C1–C2, 84.0; C4–C3–C2, 100.5; C4–C5–C6, 102.5; C1–C2–C3, 109.9; C1–C6–C5, 102.8; H1–C7–H2, 109.4; C7–C1–H3, 123.6; C7–C4–H4, 116.3; H3–C1–C2, 122.0; H3–C1–C6, 111.0; H4–C4–C3, 114.2; H4–C4–C5, 115.5; H9–C3–H10, 108.5; H7–C5–H8, 108.7; H5–C6–H6, 108.0; H11–C2–C1, 124.6; H11–C2–C3, 125.4; H2–C7–C4, 113.3; H2–C7–C1, 111.0; H1–C7–C4, 113.4; H1–C7–C1, 112.5; H9–C3–C4, 110.7; H9–C3–C2, 106.8; H10–C3–C4, 115.9; H10–C3–C2, 113.9; H7–C5–C4, 110.9; H7–C5–C6, 110.5; H8–C5–C4, 112.5; H8–C5–C6, 111.5; H5–C6–C5, 116.0; H5–C6–C1, 97.7; H6–C6–C5, 115.1; H6–C6–C1, 116.1.

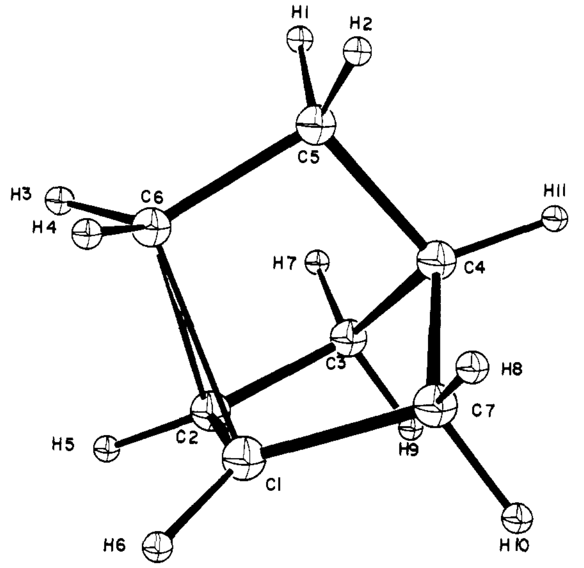

Figure 2. Optimized 4-21G geometry of the nonclassical 2-norbornyl cation, C_s symmetry. C6–C5–C4–H11 lie in the symmetry plane. Bond lengths (Å): C5–C4, 1.547; C5–C6, 1.535; C6–C1, 1.940; C1–C2, 1.384; C1–C7, 1.522; C7–C4, 1.550; C5–H2, 1.080; C6–H4, 1.080; C4–H11, 1.075; C1–H6, 1.071; C7–H8, 1.079; C7–H10, 1.085. Bond angles (deg): C6–C5–C4, 102.5; C5–C4–C7, 103.8; C3–C4–C7, 101.5; C4–C7–C1, 98.9; C7–C1–C2, 109.5; H1–C5–H2, 108.9; H3–C6–H4, 108.5; H8–C7–H10, 109.1; H2–C5–C4, 111.8; H2–C5–C6, 110.9; H11–C4–C5, 115.3; H11–C4–C7, 115.4; H4–C6–C5, 116.9; H8–C7–C4, 114.4; H8–C7–C1, 113.5; H10–C7–C4, 111.9; H10–C7–C1, 108.6; H6–C1–C7, 125.3; H6–C1–C2, 124.3; C2–C1–C6, 69.1; C1–C6–C2, 41.8.

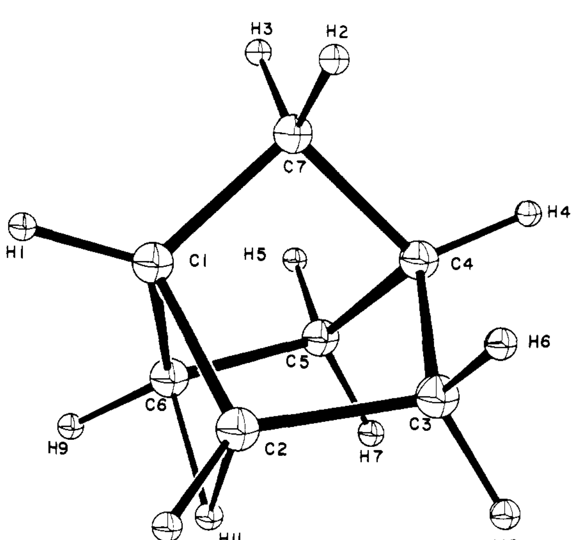

Figure 3. Optimized 4-21G geometry of edge-protonated nortricyclene, C_s symmetry. H11–H1–C1–C7–C4–H4 lie in the symmetry plane. Bond lengths (Å): C7–C1, 1.536; C7–C4, 1.546; C1–C2, 1.524; C4–C3, 1.554; C2–C3, 1.531; C7–H2, 1.080; C1–H1, 1.070; C4–H4, 1.075; C3–H6, 1.079; C3–H8, 1.082; C2–H10, 1.075; C2–H11, 1.326; C2–C6, 1.858. Bond angles (deg): C1–C7–C4, 96.3; C7–C1–C2, 105.9; C6–C1–C2, 75.1; C7–C4–C3, 101.2; C5–C4–C3, 105.3; C1–C2–C3, 106.6; C4–C3–C2, 99.3; H2–C7–H3, 109.4; H2–C7–C1, 112.0; H2–C7–C4, 113.3; C7–C1–H1, 122.2; C2–C1–H1, 119.0; C7–C4–H4, 117.0; C3–C4–H4, 115.0; H6–C3–H8, 109.2; H6–C3–C4, 114.9; H6–C3–C2, 113.4; H8–C3–C4, 111.2; H8–C3–C2, 108.4; C6–C2–H10, 125.3; C3–C2–H10, 126.6; C6–H11–C2, 88.9; C1–C2–H11, 96.7; C3–C2–H11, 100.8.

edge-protonated cyclopropane (recall the edge-protonated nortricyclene result) was significantly stabilized. The best 4-21G+d SCF results of the present work place the classical and nonclassical 2-norbornyl cations very close in energy but with the nonclassical ion $\sim$0.2 kcal/mol lower. Edge-protonated nortricyclene is predicted to be some 12 kcal/mol less stable than the classical ion at the 4-21G+d SCF level in this study.

It is necessary to estimate the effects of correlation energy differences and of solvation on the relative stabilities of these three species in order to compare the calculated results with experiment. Correlation effects[18,20,27,35,36,37] beyond the SCF level usually stabilize the bridged or nonclassical forms of small carbonium ions and often by as much as 5 kcal/mol or more. A similar stabilization of the nonclassical norbornyl cation by correlation would place it at a still lower energy than the classical isomer. Rather more approximate arguments about solvation have been made on the basis of charge localization or delocalization in the cations.[13] The lack of a clear-cut structural distinction between the classical and nonclassical 2-norbornyl cations indicated in the present work makes any quantitative pronouncement on the effects of solvation on relative energies difficult. However, the theoretical results of this study should be nearly directly comparable with any gas-phase experiments.

Structures. The optimized 4-21G geometries for the three cations are shown in Figures 1 to 3. The convergence criteria for the geometry optimization ensures that the bond lengths are precise to $\sim$0.001 Å and the bond angles to $\sim$0.1°. In making the key structural comparison between the classical and nonclassical isomers (Figures 1 and 2), it is important to note that although the carbons have been numbered consistently in the two figures, the hydrogens have not. For example, C6 in both structures is a methylene carbon interacting with the C1–C2 bond. C1, C2, and C4 are the methine units and C5, C7, C3, and C6 the methylene units in both the classical and nonclassical isomers. The classical 2-norbornyl cation is most probably a local minimum on the potential energy surface. The other two isomers were defined to have a plane symmetry and could conceivably be transition-state structures. When this symmetry constraint was removed by moving the bridging methylene group in the nonclassical ion or the bridging hydrogen in the edge-protonated form slightly out of the symmetry plane, the energy increased. This energy increase is a necessary condition for these two isomers to be a minimum. However, in the absence of a complete reoptimization of all other geometrical parameters, the increase upon a symmetry-breaking distortion is not a sufficient condition to guarantee the nature of the stationary point.

Table II. Selected Structural Features Comparisons with Previous Work

		Dewar et al.[14]	Goetz et al.[15]	Köhler–Lischka[18,28]	this work, 4-21G
classical	R(C1–C2), Å	1.468	1.438	1.478	1.406
	R(C1–C6), Å	1.586	1.632	1.605	1.753
	C2–C1–C6, deg	104.5	95.9	96.8	84.0
nonclassical	R(C6–C1), Å	1.743	1.941	1.839	1.940
	R(C1–C2), Å	1.429	1.377	1.402	1.384
edge protonated	R(C2–H11), Å	1.296		1.313	1.326
	R(C2–C6), Å	1.802		1.861	1.858

Table III. Relative C 1s Orbital Energies (eV)

	classical			nonclassical	
	Goetz et al.[a]	this work[b]		Goetz et al.[a]	this work
C2	4.58	3.70 (3.69)	C1,C2	2.48	2.47
C1	1.50	1.72 (1.72)			
C3	1.32	0.80 (0.79)	C3,C7	0.34	0.31
C6	1.08	1.63 (1.53)	C6	1.96	1.97
C4	0.58	0.45 (0.46)	C4	0.23	0.33
C7	0.39	0.23 (0.22)			
C5	0.0	0.0 0.0	C5	0.0	0.0

[a] Reference 15. [b] DZ//4-21G SCF results of this work are given in parentheses.

The carbon skeleton of the classical 2-norbornyl cation shows a number of interesting features. The C1–C2 bond length of 1.406 Å is indicative of considerable double bond character. The very long C1–C6 distance of 1.753 Å but the relatively short "nonbonded" C6–C2 distance of 2.129 Å (short relative to the predicted C5–C3 distance of 2.468 Å in this species or the experimental[29] mean next-to-bonded CC distance of 2.412 Å in norbornane) along with the very acute C6–C1–C2 angle of 84.0° in the carbonium ion face suggest that the classical ion might be viewed as unsummetrically bridged. The nonclassical and classical ions are then both bridged species and *differ in degree but not in kind.* Except for the C2–C3 distance of 1.501 Å which is typical of a C sp^2–C sp^3 bond (e.g., in propene[30] the CC single-bond length is 1.501 Å), the remaining CC bond lengths range from 1.539 Å (C1–C7) to 1.556 Å (C3–C4). Most of the CH bond lengths are approximately 1.080 Å, but there are a number of exceptions. C2–H11, C1–H3, and C4–H4 are all slightly shorter. Most notable is the long C3–H9 distance of 1.090 Å, which results from the hyperconjugative theft of electron density in this bond by the formally empty carbon p orbital on the adjacent formally carbonium ion center.

The nonclassical 2-norbornyl cation shows the bridging of the C2–C1 near double bond of length 1.384 Å by the C6 methylene group at a distance of 1.940 Å (C6–C1 or C6–C2). This bridging distance is nicely intermediate between the directly comparable C1–C6 (1.753 Å) and C2–C6 (2.129 Å) distances in the classical isomer. The other C–C single bonds vary from 1.522 Å (C1–C7) to 1.550 Å (C7–C4), while it may be recalled that in the classical structure the C1–C7 distance was 1.539 Å and the C7–C4 distance 1.547 Å. The C1–H6 bond is 1.071 Å long, reflecting the near-sp^2 hybridization of the C2 and C1 carbons. The comparable C1–H3 and C2–H11 distances in the classical isomer are 1.071 and 1.074 Å. The other CH bond lengths range from C4–H11 at 1.075 Å to C7–H10 at 1.085 Å.

In edge-protonated nortricyclene, the bridging hydrogen is 1.326 Å from C2 or C6. The C2–C6 distance is 1.858 Å. These CH and CC bonds have approximately one electron and thus are considerably longer than conventional two-electron bonds of these types. The C6–C1–C2 angle of 75.1° is equal to the value found for the analogous angle in edge-protonated cyclopropane at the STO-3G level of theory.[31]

Table II presents a comparison of certain key structural features[32] of the three isomers as calculated in this and previous[14,15,18] work. The 4-21G geometry for the nonclassical 2-norbornyl cation is in close agreement with the geometry found by Goetz, Schlegel, and Allen[15] and thus differs markedly from the MINDO/3 result.[14] For edge-protonated nortricyclene, the present calculations indicate that the bridging proton does not form quite so tight a ring structure (1.326 Å, this work; 1.296 Å, MINDO/3[14]) as predicted by the semiempirical study. For the classical form of the 2-norbornyl cation, highly significant differences arise between the structural results of the present and past calculations. The 4-21G SCF result for R(C1–C6) is ~0.15 Å longer than the values in ref 14, 15, and 18. The C2–C1–C6 angle is 11.9° smaller than that of ref 15 (95.9°) and a full 20.5° less than the MINDO/3 result[14] of 104.5°. With a decrease in this angle, the classical ion tends to bridge between C6 and C2 and thus to appear more like the nonclassical cation, in which the C6–C1 and C6–C2 distances become equal, than was found in earlier studies. Thus, the more refined theoretical treatment of this work further lessens any clear-cut distinctions between the structures of the classical and nonclassical forms of the 2-norbornyl cation. These isomers lie close in energy but also are closer in geometry than has previously been indicated. Recent experimental work[6] on 2-adamantyl and other cations has been interpreted as showing no sharp distinction between the categories of "classical" and "nonclassical" carbocations. Some cations were indicated to be intermediate in character (e.g., they may be unsymmetrically bridged). The most extensively studied carbonium ion, the 2-norbornyl system, is also not easily categorized as classical or nonclassical.

As is illustrated by the relative C 1s orbital energies given in Table III, the "bridging" interactions in the classical form does have noticeable effects on the properties of this species. From ref 15, the C2 and C1 1s orbital energies (which become equal in the nonclassical species) differ by 3.08 eV while for the 4-21G geometry of this work the difference is significantly reduced to 1.98 eV. However, the close agreement between this earlier[15] and the present work for the relative C 1s orbital energies of the nonclassical 2-norbornyl cation should also be noted.

The view presented that the classical 2-norbornyl cation may be partially or unsymmetrically bridged has support in the literature. P. v. R. Schleyer has noted[33] that "there is nothing wrong with partially bridged ions from a theoretical viewpoint. There should be a continuum from hyperconjunction without significant motion toward bridging, to unsymmetrical bridging, to symmetrical bridging" and that STO-3G calculations[31] indicate that the methyl-eclipsed propyl cation (analogous to the classical norbornyl cation), with a CCC angle of 83° in the carbonium ion face, is partially bridged. However, in the case of the propyl cation, split-valence and polarized calculations[34,36] suggested a collapse of this species.

Concluding Remarks

At a consistently higher level of theory than was previously available, this study confirms much earlier work on the relative SCF energies of the classical, nonclassical, and edge-protonated forms of $C_7H_{11}^+$. Correlation effects extrapolated to the norbornyl system from smaller carbocations indicate a preferential stabilization of the nonclassical and edge-protonated isomers beyond the Hartree–Fock level. In contrast to the energetics, the structure found for the classical ion in the present calculations is somewhat at variance with earlier work and implies that the classical 2-norbornyl cation might best be viewed as an unsymmetrically bridged species.

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