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An ab Initio Molecular Orbital Study of the 2-Adamantyl Cation

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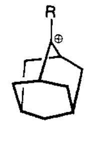
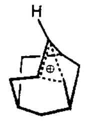
Abstract: The 2-adamantyl cation is found by ab initio molecular orbital calculations to have an unsymmetrical C_s symmetry ground state and the "classical" C_{2v} symmetry is found to be a transition state, although the potential energy surface is extremely flat (8.47 kJ/mol separate the structures at the MP2 6-31G*//6-31G* + ZPVE 6-31G level). The ground-state C_s structure involves a very significant distortion from the classical cation, this distortion involving a bending of the C_α–C^+–C_α bridge toward one face of the cation (17.3°), a further pyramidalization of the C^+–H bond in the same direction (11.1°), and very unequal C_α–C_β bond lengths (1.542 and 1.603 Å). These results can be interpreted in terms of "enhanced C–C hyperconjugation" but are not consistent with the usual concept of "bridging" in carbocations. Carbon NMR chemical shifts have also been computed for the 2-adamantyl cation and these show a remarkable consistency with previously published experimental NMR data for the tertiary 2-adamantyl cation. The computational results have also been used to reinterpret gas-phase ionization data for the 2-adamantyl radical, and their significance relative to the numerous solvolysis studies of this system is discussed. The 1-adamantyl cation is calculated to be 53.02 kJ/mol more stable than the 2-adamantyl structure, in reasonable agreement with the experimental data.

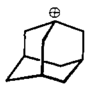
The solvolysis of 2-adamantyl derivatives has been extensively studied because this system is widely regarded to involve a pure k_c mechanism[1,2] (independent of nucleophile, no solvent participation or anchimeric assistance in the rate-determining steps). The structure of the resulting cation intermediate **1** has been described as weakly σ-bridged, i.e. **1a**, by some authors[3,4], although in other cases the presence of a "normal" secondary cation is implied.[5,6]



1: R = H
2: R = methyl



1a



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The gas-phase 2-adamantyl cation is also known, both from mass spectrometry[7] and from recent studies involving ionization of the 2-adamantyl radical.[8] The latter results have some potential

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(3) The following references relate to "bridging" in carbocation **1** and also 1-R-2-adamantyl and/or tertiary protoadamantyl cations. The evidence for bridging is much stronger in these latter two cases, although arguments to the contrary have appeared.[4] Because of the number of heavy atoms and lack of symmetry, we have not attempted theoretical calculations on, for example, 1-methyl-2-adamantyl cation. (a) Sinnott, M. L.; Storesund, H. J.; Whiting, M. C. *J. Chem. Soc. D* **1969**, 1000. (b) Faulkner, D.; McKervey, M. A.; Lenoir, D.; Senkler, C. A.; Schleyer, P. v. R. *Tetrahedron Lett.* **1973**, 705. (c) Storesund, H. J.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1452. (d) Bone, J. A.; Pritt, J. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1447. (e) Lenoir, D.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 2138. (f) Lenoir, D.; Raber, D. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 3149. (g) Lenoir, D.; Mison, P.; Hyson, E.; Schleyer, P. v. R.; Saunders, M.; Vogel, P.; Telkowski, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 2157. (h) Lenoir, D. *Chem. Ber.* **1973**, *106*, 2366. (i) Pritt, J. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1458. (j) Nordlander, J. E.; Haky, J. E.; Landino, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 7487. (k) Nordlander, J. E.; Haky, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 1518. (l) Kovačevič, D.; Goričnik, B.; Majerski, Z. *J. Org. Chem.* **1978**, *43*, 4008. (m) Gassman, P. G.; Saito, K.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 7615. (n) Cheung, C. K.; Tseng, L. T.; Lin, M.-H.; Srivastava, S.; LeNoble, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 1598. (o) Grob, C. A.; Wittwer, G.; Rama Rao, K. *Helv. Chim. Acta* **1985**, *68*, 651. (p) Banert, K.; Kurnianto, A. *Chem. Ber.* **1986**, *119*, 3826. (q) Banert, K.; Bunse, M.; Engbert, T.; Gassen, K.-R.; Kurnianto, A. W.; Kirmse, W. *Recl. Trav. Chim., Pays-Bas* **1986**, *105*, 272.

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(5) Several authors in various ref 1 citations emphasize that a k_c rather than k_Δ mechanism is involved in the solvolysis and they see no need to invoke a bridged intermediate. The retention of configuration in solvolysis is regarded as an ion-pairing phenomenon.

(6) Correlations of solvolysis rate constants with molecular mechanics strain energies invariably involve a planar cation. (a) Smith, M. R.; Harris, J. M. *J. Org. Chem.* **1978**, *43*, 3588. (b) Müller, P.; Mareda, J. *Tetrahedron Lett.* **1984**, *25*, 1703. (c) Müller, P.; Blanc, J.; Perlberger, J. C. *Helv. Chim. Acta* **1982**, *65*, 1418. (d) Müller, P.; Mareda, J. *Helv. Chim. Acta* **1985**, *68*, 119.

(7) Wesdemiotis, C.; Schilling, M.; Schwartz, H. S. *Angew. Chem.* **1979**, *91*, 1017.

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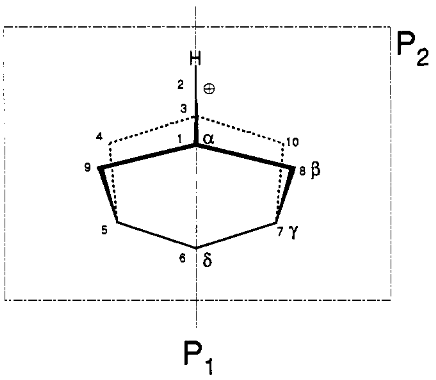

Figure 1. C_{2v} symmetry for the 2-adamantyl cation **1**, with arbitrarily defined planes P_1 and P_2 (view down the P_1 plane).

structural information that will be discussed later. Cation **1** can also be generated in inert (non-nucleophilic) solvents by photolysis of the corresponding iodide.[9]

Attempts to prepare the observable cation **1** in superacid media have all failed,[10] only the 1-adamantyl cation **3** being detected. The observable 2-methyl-2-adamantyl cation **2** has long been known[11] and has been considered a typical tertiary aliphatic carbocation. Recently, however, ^{13}C NMR results involving unsymmetrically substituted analogues of **2** were interpreted in terms of two structural isomers, each postulated to involve preferential and enhanced hyperconjugation with a particular face of the cation framework.[12] A key experimental observation here was that the barrier for the isomer interconversion had to be very small, certainly less than 20 kJ/mol (and possibly much smaller). Assuming that the planar cation represented the transition state, it was obvious that one was dealing with a rather flat potential energy surface, a situation notoriously characteristic of carbocations in general, but not a situation one would have necessarily expected for **2** (or **1**) with the apparently rigid interlocking rings.

Molecular mechanics calculations involving **1** have been reported[13] and, not surprisingly, produce a normal sp^2-hybridized cation. Of more importance, the resulting calculated strain energy for **1**, and numerous other cations, correlates quite well with the respective solvolysis rate constant data.

Semiempirical MO calculations[14] (MINDO/3, MNDO, AM1) of **1** (or **2**) show no particularly remarkable features. With no enforced symmetry, these calculations optimize to a near perfectly planar cation. Relative to a hydrocarbon, the $C^+–C_\alpha$ bonds (see Figure 1 for the designation of α, β, etc.) are shortened (1.491, MNDO; 1.478 MINDO/3; 1.461, AM1) and the $C_\alpha–C_\beta$ bonds are elongated by hyperconjugation (1.575, MNDO; 1.567, MINDO/3; 1.552, AM1), both results expected for a symmetrical cation structure. Attempts to locate a bridged structure **1a** as a local energy minimum on the semiempirical potential energy surface also failed (see later).

Because of the considerable intrinsic interest in the structure of **1** and also because of our specific interest in the solution structures associated with the tertiary cation **2**, we decided to carry out a detailed ab initio MO study of **1**. The 1-adamantyl cation **3** has also been computed, principly so that an energy difference between **1** and **3** can be obtained.

Method

All calculations were carried out using either the GAUSSIAN 82[15] or the GAUSSIAN 86 system.[16] Geometry optimization was undertaken by using the analytical gradient algorithms and internal basis sets. The exact procedures followed are described in the following section. An estimate for the correction for the effect of electron correlation was obtained at the 6-31G basis set level and with the geometry optimized at the same level. Semiempirical MINDO/3[17a] and MNDO[17b] results were obtained with the MOPAC package,[18] while AM1[17c] calculations were carried out with the GAUSSIAN 86 implementation. Calculations of ^{13}C NMR chemical shifts were performed with the IGLO program[19] with the small internal gaussian lobe basis. This basis is approximately equivalent to the 4-31G split level basis of the GAUSSIAN programs.

Ab Initio Calculations

At the STO-3G minimal basis set level, the optimized "symmetrical" structure (C_{2v} symmetry, planes P_1 and P_2 defined as shown in Figure 1) corresponded to a transition state (one imaginary frequency or negative force constant). This imaginary frequency was almost entirely associated with an out-of-plane P_1 bending mode of the $C^+–H$ bond and was also small (116.8i cm^{-1}). Relaxing the symmetry at the STO-3G level (removal of the P_1 plane, giving overall C_s symmetry) and starting from a very slightly distorted structure, one finds an apparent optimized geometry that is to all intents a "symmetrical" structure, with an energy of only 1.3 J/mol below the transition state and with negligible geometry changes. However, starting from a less-symmetric geometry, one finds a second and lower energy minimum[20] which is considerably more distorted in terms of the original P_1 plane. These distortions involve three main considerations: (1) a bending of the $C_\alpha–C^+–C_\alpha$ bridge toward one face of the cation; (2) a further bending (pyramidalization) of the $C^+–H$ bond out of the $C_\alpha–C^+–C_\alpha$ plane, again toward the same face; and (3) a difference in the bond lengths of the $C_\alpha–C_\beta$ bonds, with the longer bonds involving the face toward which the distortions are occurring.

A defined reference for these asymmetries, along with the actual values for bonds and angles, for various basis sets, is given in Table I. The energy difference between the C_s and C_{2v} structures is reported in Table II.

A considerable effort was made to ensure that the C_s minimum was a global minimum for the molecule at this level of calculation, and indeed, optimization at the STO-3G level with no imposed symmetry gave the same minimum. Three separate and quite asymmetric geometries were used as input in these computations. Since one of the structures previously proposed for **1** involves the concept of a "weak bridge" between C2 and C4 (**1a**), we artificially and arbitrarily constructed the geometry shown as structure **1a′**. This structure with three fixed bond lengths was first "optimized"[21] at the AM1 semiempirical level and then used as an input in the STO-3G computation, but, as indicated earlier, this geometry collapsed to the C_s symmetric structure already discussed. If one removes the fixed bond lengths in the AM1 calculation, one also

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(8) Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162.

(9) Kropp, P. J.; Gibson, J. R.; Snyder, J. J.; Poindexter, G. S. *Tetrahedron Lett.* **1978**, 207.

(10) See footnote 3 of ref 12a. Also, Sunko, D. E.; Abstract from "International Symposium on Carbocations and Other Related Reactive Intermediates", Tübingen, Germany, Aug. 18–19, 1988, has reported negative results using very low temperature IR measurements.

(11) Olah, G. A.; Liang, G.; Mateescu, G. D. *J. Org. Chem.* **1974**, *39*, 3750.

(12) (a) Finne, E. S.; Gunn, J. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7816. (b) Kirchen, R. P.; Ranganayakulu, K.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7811.

(13) See ref 6. A fairly rigid out-of-plane deformation potential is used for the carbocation moiety.

(14) Paquette, L. A.; Kobayashi, T.; Kesselmayer, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 6568, have independently computed the 2-adamantyl cation using MNDO and AM1 basis sets.

(15) Binkley, J. S.; Frisch, M. J.; De Frees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.

(16) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, L. R.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh PA, 1984.

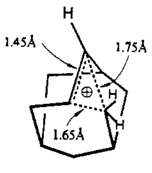
(17) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4499. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (c) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(18) Dewar, M. J. S.; Stewart, J. J. P. QCPE publication 455, Department of Chemistry, Indiana University, Bloomington, IN 47405.

(19) (a) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1819. (b) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020. (c) Bremer, M.; Schleyer, P. v. R.; Schötz, K.; Kaush, M.; Schindler, M.; *Agnew. Chem.* **1987**, *99*, 795. (d) Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300. (e) Laidig, K.; Saunders, M.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652. (f) Bremer, M.; Schleyer, P. v. R.; Fleischer, U. *J. Am. Chem. Soc.* **1989**, *111*, 1147.

(20) We regard the "symmetric minimum" as an artefact of the minimal basis set, since it was not encountered in the higher level calculations.

(21) This structure did not completely optimize, but the energy changes were very small at the stage where the computation was terminated.



1a

gets reversion to the same totally symmetric (C_{2v}) structure referred to previously.

An indication of how bad this artificially constructed and partially optimized bridged cation is can be seen in the energy difference at the STO-3G level (>100 kJ/mol). We are thus fairly confident that an energy minimum corresponding to a bridged ion does not exist at the STO-3G level of computation.

The single point 3-21G//STO-3G and 6-31G//STO-3G energy differences for the C_{2v} and C_s structures were larger than for the STO-3G//STO-3G results (see Table II), suggesting that the extended basis sets were accentuating the asymmetry associated with the C_s cation structure.

Geometry optimization at the split valence 6-31G level bore this out. The C_s structure is about 2.8 kJ/mol below the C_{2v} structure and is much more distorted (see Table I).[22] Optimization at the 6-31G* level increases the energy difference to 5.1 kJ/mol and further increases the asymmetry of the C_s structure compared to the unpolarized basis set (Tables I and II). The 6-31G geometry was used for a 6-31G-MP2//6-31G calculation of the correlated energy difference between the C_{2v} and C_s structures (Table II), showing that correlation favors the C_s structure. A frequency analysis was also carried out for the 6-31G basis set, confirming that the C_{2v} structure is still a transition state and the C_s structure an energy minimum. The relative zero point energy (ZPVE) correction of 0.873 kJ/mol favors the C_{2v} structure (Table II).

The use of C_s symmetry in these high-level calculations poses some problems. In the case of the STO-3G results, one can show with reasonable certainty that the C_s structure is a global minimum. With the 6-31G calculations, the C_s structure is at least a local minimum. However, the frequencies calculated for this C_s structure reveal a number of low-frequency modes that might signify some small barrier transition state leading to a lower energy asymmetric structure (such as **1a**, for example). Computed frequencies less than 500 cm^{-1} are listed in Table III and correlated with the same vibrations calculated with the STO-3G basis set. Those with an A″ designation represent asymmetric vibrations with respect to the C_s plane. The lowest frequency mode in the 6-31G calculation is indeed an A″ type and the atom displacements involved here are shown in Figure 2. Although this skeletal rocking motion does alternately move a β-carbon slightly closer to the C$^+$ center there is no relative movement of the C_α–C$^+$–C_α centers. In order to assess whether these low frequencies were unique to the cation or were a characteristic of the molecular skeleton, a 6-31G geometry optimization and frequency calculation was carried out on adamantane itself.

The seven lowest frequencies in adamantane (Table III) are indeed quite small and have T_1, A_2, and T_2 designations. In C_s symmetry, the triply degenerate T_1 and T_2 modes transform into 2A″, A′ and 2A′, A″, respectively, while A_2 becomes A″. Thus the low frequencies found in **1** are seen to be characteristic of the adamantane ring and do not originate as a consequence of some aspect of the cation structure.

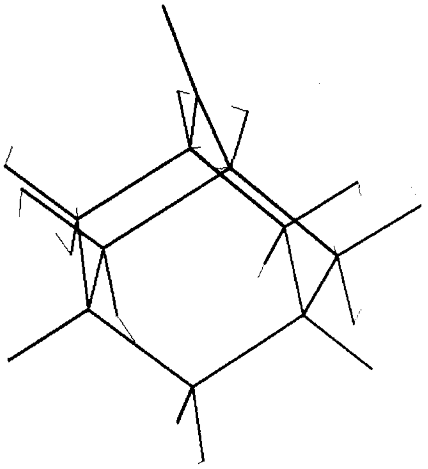


Figure 2. Lowest frequency mode (243.4 cm^{-1}, A″ type) for the C_s structure of **1** (6-31G basis set). The thin lines represent the atom displacement vectors but some of those for carbons are obscured. The displacements are essentially "group" motions, i.e. CH$_2$, and involve a complex rocking movement.

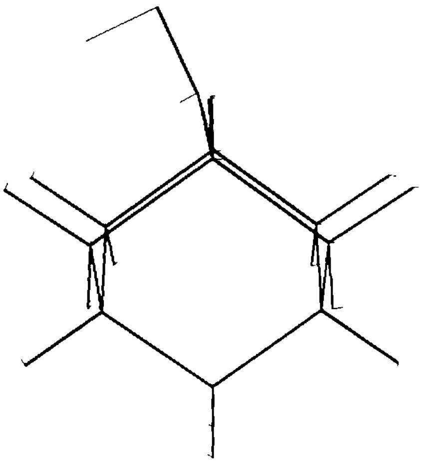


Figure 3. The second lowest frequency mode (297.6 cm^{-1}, A′ type) for the C_s structure of **1**. By far the largest displacements involve the C$^+$–H bond and the C_α–C$^+$–C_α bridge.

The remaining A′ mode at 297.6 cm^{-1} (Table III) found for **1** is however unique to the cation and represents mainly the in-plane movement of the C$^+$–H bond and the C_α–C$^+$–C_α bridge (Figure 3). This vibration would make a significant contribution to the transition state leading to the degenerate isomerization of the C_s cation (the asymmetric C–C stretching modes of the C_α–C_β bonds would also be involved).

A remaining uncertainty involves the possibility of an asymmetric minimum on the correlated potential energy surface. A single-point 6-31G-MP2 calculation was carried out by displacing atoms (one-tenth of the normalized Cartesian displacement vector) along the normal mode of the lowest frequency A″ vibration (see Figure 2). The resulting carbon atom displacements of about 0.01–0.015 Å led to an SCF energy of 0.26 kJ/mol above the C_s minimum, and an MP2 correlated energy of 0.04 kJ/mol above the correlated C_s minimum. Correlation is certainly flattening the computed out-of-plane (P$_2$) potential energy surface in the C_s structure, but like the SCF potential surface, there is no particular indication that one might actually have an asymmetric ground state on the MP2 surface.[24]

The Calculated Geometry of 1. Correlation with Experiments

Perhaps the most unexpected finding in this work is the very flat potential energy surface in **1** for what amounts to quite significant spatial distortions. Thus, the C$^+$–H hydrogen can move in an arc of approximately 50° about the C_α–C_α axis with very little change in energy. Much of this movement involves the

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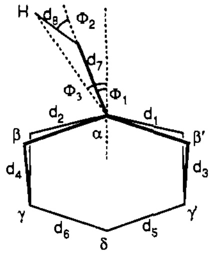
[22] Any details of these calculations are available from the authors. Many geometric parameters are "normal", e.g., the C_s structure shows a C_α–C$^+$–C_α angle of 119.7° vs 118.8 in the C_{2v} case. The corresponding C_β–C_α–C_β angles are 109.0° and 108.6° (all 6-31G* structures).

[23] Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 269.

[24] When a unit-normalized Cartesian displacement of this lowest A″ mode was computed, the SCF energy went up by 35.5 kJ/mol and the MP2 energy went up by 13 kJ/mol. Thus both surfaces look to be continuously rising in energy along this A″ mode.

Table I. Geometries of the C_s and C_{2v} Structures of **1**



C_s Structure

basis set	Φ_1[a]	Φ_2[a]	Φ_3[a]	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
STO-3G	8.2	7.1	12.4	1.560	1.582	1.546	1.546	1.547	1.547	1.495	1.108
6-31G	15.0	95	20.65	1.547	1.613	1.537	1.534	1.540	1.539	1.454	1.079
6-31G*	17.3	11.1	23.9	1.542	1.603	1.534	1.531	1.536	1.537	1.451	1.080

C_{2v} Structure

basis set	d_1,d_2	d_3,d_4	d_5,d_6	d_7	d_8
STO-3G	1.571	1.546	1.547	1.498	1.108
6-31G	1.577	1.535	1.538	1.460	1.079
6-31G*	1.569	1.532	1.535	1.460	1.080

[a] This angle is measured relative to a plane that bisects the ααβ and ααβ' planes.

Table II. Calculated and Relative Energies of 2-Adamantyl **1** and 1-Adamantyl **3** Cations

	2-adamantyl **1**				1-adamantyl **3**	
	energy (hartree)				energy (hartree)	
method[a]	C_{2v}	C_s	C_1[c]	ΔE (kJ/mol)	C_{3v}	ΔE[b] (kJ/mol)
SCF STO-3G//STO-3G	−382.678 280	−382.678 381		0.27		
SCF 3-21G//STO-3G	−385.026 778	−385.027 420		1.69		
SCF 6-31G//STO-3G	−387.000 092	−387.000 611		1.36		
SCF 6-31G//6-31G	−387.003 100	−387.004 167	−387.004 061	2.80 (0.26)[d]	−387.020 589	−43.13
SCF 6-31G*//6-31G*	−387.162 516	−387.164 458		5.10		
MP2 6-31G//6-31G	−387.879 744	−387.882 423	−387.882 407	7.04 (0.04)[d]	−387.903 276	−54.77
MP2 6-31G*//6-31G[e]				9.34[e]		
ZPVE 6-31G//6-31G	649.99[f]	650.96[f]		−0.87[g]	652.90[f]	1.75[g]
MP2 6-31G+ZPVE 6-31G				5.46[g]		−53.02
MP2 6-31G*+ZPVE 6-31G				8.47[e,g]		

[a] The notation xxxx//yyyy means that the calculation was performed using basis set xxxx on the geometry optimized at the SCF level with basis set yyyy. [b] Relative to **1** with C_s symmetry. [c] Obtained by adding 0.1 times the normalized Cartesian displacement vectors for the lowest frequency normal mode (A″ symmetry) to the C_s geometry. [d] $E(C_1) - E(C_s)$. [e] Estimated by adding the 6-31G MP2 correlation correction to the 6-31G* SCF energy difference. [f] kJ/mol. [g] The ZPVE difference has been multiplied by 0.9 to correct for the systematic error in calculated frequencies.[23]

Table III. Vibrational Frequencies of 2-Adamantyl Cation **1** and Adamantane (<500 cm^{-1})[a]

2-adamantyl **1**						adamantane	
C_s				C_{2v}		T_d	
STO-3G		6-31G		6-31G		6-31G	
A′	164.4	A″	243.4	B1	241.7i		
A″	283.6	A′	297.6	A2	274.5		
A″	331.5	A″	323.3	B2	320.3	T1	340.3
A′	399.9	A′	394.8	B1	386.7		
A″	442.8	A″	402.4	A2	427.3	A2	438.5
A′	451.9	A′	448.3	A1	435.0		
A′	480.8	A′	476.2	A1	476.0	T2	481.3
A″	481.1	A″	477.5	B2	477.8		

[a] Since a harmonic approximation is used in the calculation, one should not put an over reliance on the actual numbers.

associated shifting of the C$^+$ carbon bridge. Although the computed C_s ground-state structure is very distorted, the "classical" C_{2v} geometry is also stabilized and only just misses out being the ground state.

Beauchamp[8] has studied the gas-phase ionization of the planar 2-adamantyl radical[25] and obtained an unexpectedly large energy distribution (line width) for this Franck–Condon process. This was tentatively rationalized by considering that the planar radical had bond angles that differed from the classical 120° angles of an assumed rigid planar secondary cation structure. The present

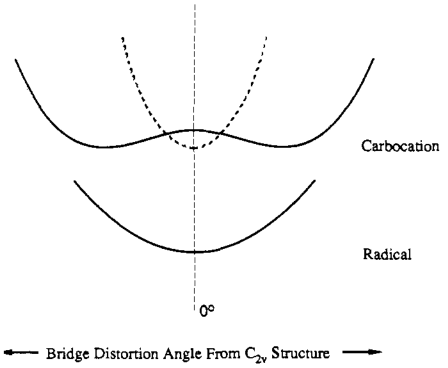


Figure 4. Schematic representation of the vertical ionization process in the 2-adamantyl radical (solid lines). No determination of the actual radical potential surface has been computed but we assume from the experimental work that a planar structure is involved. The previous tentative assumption[8] of a rigid secondary cation potential is qualitatively shown as a dashed line. In either case one might anticipate a broad energy distribution, since the two surfaces in each case are shown as different, but the current results favor the solid line explanation.

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(25) Kira, M.; Watanabe, M.; Ichinose, M.; Sakurai, H. *J. Am. Chem. Soc.* **1982**, *104*, 3762.

calculations suggest of course a completely different interpretation, as shown in Figure 4. This figure does not show the additional geometry change involving the C_α–C_β bonds and would actually underestimate the total effect.

The hydrogen/deuterium kinetic isotope effects have been reported for both the *1-d* (β-isotope)[26] and *2-d* (α-isotope)[27] 2-adamantyl esters. Although the latter is quite large (k_H/k_D = 1.225 ± 0.001), the former (k_H/k_D = 1.029 ± 0.005) is considered to be more relevant from the structural viewpoint. For a planar cation intermediate one might have expected a slightly inverse k_H/k_D value, ca. 0.985, and on this basis Sunko[27] made several possible rationalizations, including that of an sp^3-hybridized cationic transition state. In terms of the figure in Table I, this would mean a θ_2 angle of 60°. The most distorted value of θ_2 is 11.1°, which is much closer to sp^2 than sp^3. However, the total angle represented by θ_3 (23.9°) may be the more important parameter in evaluating this β-deuterium isotope effect using Sunko's equation.

In order to roughly compare our computational data with the literature kinetic isotope data, we have calculated the effect on the zero-point energies for the presence of a deuterium atom at each unique position in both the C_s and C_{2v} gas-phase cations.[28] These ZPE values were compared to those for a reference adamantane system (6-31G structure optimization and frequency calculation, substituting for one hydrogen at C2 by an infinite mass and placing a mono-deuterium in each unique position).[29] The transition state for a rate-limiting k_c solvolysis should partially resemble the product (i.e. the cation, or more correctly, a cation-leaving group ion pair). The results of the ZPE calculations are in reasonable accord with the experimental k_H/k_D values. As expected, the α-D substitution (at C^+) results in by far the largest ZPE difference (predicting a "normal" k_H/k_D, as found), but this calculated value is large for both the C_s and C_{2v} structures (545 and 912 J/mol, respectively) and one cannot really use these numbers for a structural determination. The β-D substitution (at C_α in **1**) results in a much smaller ZPE difference, but the effect is noticeably larger in the C_{2v} structure (−183 J/mol), with the prediction of a considerably larger "inverse" isotope effect than for the C_s structure (−110 J/mol),[30] i.e. as also predicted from Sunko's equation. The experimental value of a slightly "normal" k_H/k_D = 1.029 ± 0.005 is thus partially consistent with the ZPE calculations based on the C_s structure.

Interpretation of the Asymmetric C_s Structure on Molecular Orbital Terms

In experimental work involving the tertiary 2-methyl-2-adamantyl cation **2**, it was suggested[12] that the structure of **2** in superacids involved preferential C–C hyperconjugation on one face (or the other) of the ring system. It was also suggested that such preferential hyperconjugation would involve some nonplanarity at the C^+ center (and indeed that this nonplanarity would increase the overlap of the C^+ p orbital with the C_α–C_β bonds on the face toward which the distortion takes place). The structure found for **1** partly bears out these predictions; however, we did not anticipate that the C_α–C^+–C_α bridge would distort. One must also concede that these calculations are for a secondary cation and so the effects are likely to be accentuated compared to those for **2**.

To show the extent to which the C_α–C_β bonds interact with the C^+ orbital, we plot in Figure 5 the LUMO orbital for both the C_s and C_{2v} geometries. The LUMO orbital is pictured because the corresponding bonding interaction is distributed among several MO's and is not as easily depicted. One clearly sees that the hyperconjugative interaction in the C_s structure is almost entirely on one face of the molecule. This same degree of hyperconjugative specificity is necessarily present in the various HOMO orbitals and this of course accounts for the marked differences seen in the C_α–C_β bond lengths (Table I).

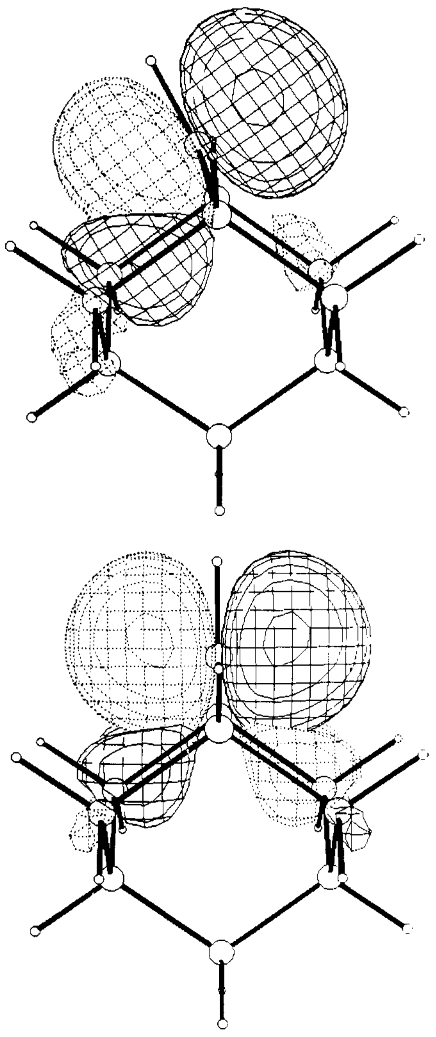
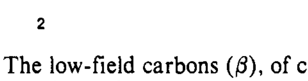


Figure 5. (a) The LUMO orbital for the C_s structure of **1** (6-31G*); (b) the LUMO orbital for the C_{2v} structure of **1** (6-31G*).

In both the C_s and C_{2v} structures there is extensive C–C hyperconjugation and, as stated previously, the preferential hyperconjugation in the C_s structure is just slightly better in energy terms than the more extended double hyperconjugation in the C_{2v} structure.

A Correlation of the Theoretical Results for 1 with ^{13}C NMR Shift Data for 2

In 2-methyl-2-adamantyl cations, the key data that led to the postulate of equilibrating, "enhanced C–C hyperconjugation" structures was a temperature dependence in the ^{13}C chemical shifts for the β-carbons. It was estimated that the two faces of cation **2** would have β-carbon chemical shifts as shown below:



2

δ_β = 65.5 ppm
$\delta_{\beta'}$ = 36.5 ppm
$\Delta\delta$ = 29.0 ppm
av = 51.0 ppm

The low-field carbons (β), of course, are assumed to be those where the preferential hyperconjugation is occurring (the longer C_α–C_β bonds).

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[26] Shiner, V. J., Jr.; Fisher, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 2553.

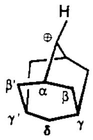
[27] Sunko, D. E.; Szele, I.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 5000.

[28] The detailed data are available on request.

[29] This model is not perfect for an α-deuterium isotope calculation, where the leaving group undoubtedly has some polar effect on the adjacent C–D bond. However, for the more remote deuteriums, it is likely to be satisfactory.

[30] Very remote deuterium atoms (e.g. on C6) have a value of about −100 J/mol in our scheme, a number that we regard as an artefact of the computational assumptions. Numbers of this order should then be regarded as consistent with k_H/k_D = 1. Thus −183 J/mol is indicative of a predicted small inverse isotope effect, whereas −100 J/mol is indicative of $k_H/k_D \sim 1$.

Table IV. Calculated[a] ^{13}C NMR Chemical Shifts[b] for **1**



atom	C_{2v} structure	C_s structure
C^+	368.7	334.0
C_α	53.5	54.8
C_β	41.9	51.7
$C_{\beta'}$		28.3[c]
C_γ	14.4	14.7
$C_{\gamma'}$		12.5
C_δ	26.2	25.9
$\sum\delta$ ^{13}C (for all carbons)	698.7	656.7

[a] Calculated using 6-31G* geometries and the IGLO program.[19] [b] The IGLO calculation also gives the ^{1}H chemical shifts. The chemical shift of the proton attached to the cationic center is calculated at δ 18.75 in the C_{2v} structure and δ 16.89 in the C_s structure. [c] $\delta C_\beta - \delta C_{\beta'} = 23.4$ ppm.

As previously noted, the secondary 2-adamantyl cation **1** has not yet been observed in superacids. One can however calculate chemical shifts for the carbons in **1** using the IGLO method,[19] which has already been shown to give realistic values for many carbocations. The computed chemical shifts for both the C_s and C_{2v} structures of **1** are given in Table IV. Although the calculated $\Delta\delta$ diference for the β and β' carbons in the C_s structure (6-31G* geometry) of **1** is somewhat smaller than the experimental results for **2** (see above), we still regard this correspondence as remarkably good and in fact a nice vindication of the original experimental interpretation for the tertiary 2-adamantyl cations. It is worth noting that solvation effects in the tertiary cations **2** may well accentuate the asymmetry of the structure, compared to data for the gas-phase **1** (i.e. the calculated data). Note also that the small barrier computed for the interconversion of the two C_s structures (Table II) would not allow one to "freeze-out" a single C_s structure on the NMR time scale at any "reasonable" temperature. A similar experimental conclusion was reached in the case of the tertiary 2-methyl-2-adamantyl cation results.

Kelly[31] has also prepared the superacid 2-methyl-2-adamantyl cation **2** and has concluded from an analysis of the $J_{^{13}C_2-H}$ coupling constant that the cation deviates from the classical sp^2-hybridized structure.

Olah, Schleyer, and co-workers[32] proposed some years ago that the difference between the $\sum\delta^{13}$C shifts for a cation and neutral precursor provided a test for whether a cation was classical or nonclassical. As shown in Table IV, this criteria does not distinguish appreciably between the C_s and C_{2v} structures for **1**, and indeed both fit into the "classical" category if one compares these summed chemical shifts to those of adamantane. This point is discussed further in the next section.

Correlation with Solvolysis Results

It has been proposed that the intermediate in 2-adamantyl solvolysis is a "weakly bridged" carbocation structure.[3] Two of the points of evidence are retention of configuration in solvolysis and the formation of small amounts of protoadamantane products. Although we reiterate the proviso that one is not computing the structure of solution carbocations (or ion pairs), we suggest that one should now uncouple these arguments, i.e. that they do not arise from some common phenomenon.

The retention of configuration in solvolysis is nicely accommodated in the calculated C_s structure for **1**. Under conditions where the solvolysis intermediate is longer lived, one then has a competition between nucleophile capture and cation inversion, and this predicted behavior is roughly in accordance with experimental results.

The bridged structure for **1** is generally depicted as shown in **1a**.[33] There is an analogy implied here to the bridged 2-norbornyl cation, with C4(Cβ) in **1a** being partially pentacoordinate and corresponding to C6 in the 2-norbornyl case. Such pentacoordinate bonding usually results in ^{13}C chemical shifts that are higher field that normal.[32] The computed chemical shifts for the hyperconjugating β carbons in **1** (C_s) clearly show just the opposite behavior, but one entirely consistent with a simple hyperconjugation picture. Thus, the difference between our computed C_s structure for **1** and the bridged structure **1a** goes much deeper than mere semantics (see recent ref 34 for a related discussion of this point).

Traylor[35] has sought to differentiate between hyperconjugation and bridging, but the kind of hyperconjugative interaction seen in **1** (i.e. extensive displacement of atoms from an idealized sp^2-hybridized structure) is not easily defined in his terms.

Relationship between 1 and the 1-Adamantyl Cation 3

A 1,2-hydride shift in **1**, to give the tertiary cation **3**, is not observed experimentally and must correspond to a very high transition-state barrier.[36] The explanation of this high barrier generally assumes a planar cation for **1** and then points out the ca. 90° unfavorable overlap angle between the migrating C_α–H bond and the C^+ p orbital.[37]

We believe that this same argument still holds, since the C_α–H bond and the C^+ orbital in the C_s structure of **1** still retain this same poor overlap angle. Since we have obtained high-level computed energies for **1**, we decided to also determine as accurately as possible the energy difference between **1** and **3**. The energy of the 1-adamantyl cation **3** (C_{3v} symmetry) was obtained at the 6-31G-MP2//6-31G level.[34] The geometry in this case is not greatly different from that obtained earlier with partial STO/3G optimization.[35] The calculated energy difference between **1** and **3**, with zero-point energy corrections included (6-31G level), is 53.02 kJ/mol favoring **3**. These data can be compared with the experimental estimate[8] of 39.7 kJ/mol favoring **3** (the large error limits given in this work would actually cover our calculated value).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for generous financial support. We are also very grateful to Drs. Michael Schindler and U. Fleischer, University of Bochum, West Germany, for a copy of the IGLO program.

Registry No. 1, 21410-12-8; **3**, 19740-18-2; deuterium, 7782-39-0; adamantane, 281-23-2.

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(31) Private communication: Kelly, D. P. Department of Organic Chemistry, University of Melbourne, Melbourne, Australia.

(32) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Surya Prakash, G. K.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

(33) Grob[30] has described the bridging (or delocalization) as symmetrical and has depicted this by using two dashed lines, one each from the C^+ center to the individual β carbons on one face of the cation. To the extent that dashed lines indicate partial bonding, then this picture is not consistent with the calculations reported here.

(34) Lin, M.-H.; Cheung, C. K.; le Noble, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 6562. See also ref 3n.

(35) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715.

(36) Vogel, P.; Saunders, M.; Thielecke, W.; Schleyer, P. v. R. *Tetrahedron Lett.* **1971**, 1429. See also ref 1d for an even earlier discussion of this point.

(37) Dutler, R.; Rauk, A.; Sorensen, T. S.; Whitworth, S. M. Unpublished results.

(38) Sunko, D. E.; Hirsl-Stareevic, S.; Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6163.