Theoretical Study of the $C_{12}H_{17}^+$ Ion Potential Energy Surface in the 2,3-Dimethyl-3-phenyl-2-butyl Cation Region

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The region of the $C_{12}H_{17}^+$ potential energy surface (PES) defined by the 2,3-dimethyl-3-phenyl-2-butyl cation and its rearranged isomers produced by 1,2-methyl and 1,2-phenyl shifts was studied through SCF-MO calculations. AM1, HF/3–21G, and HF/6–31G* geometries were found for key structures of this PES. HF/3–21G and HF/6–31G* transition state structures (TSs) were found for both the 1,2-methyl (**5-rot-TS**) and the 1,2-phenyl shift (**5-TS**). Frequency calculations were performed on the latter TSs and the HF/3–21G and HF/6–31G* initial states (ISs), C_s 2,3-dimethyl-3-phenyl-2-butyl cation (**5**), the rotamer of **5** with a methyl group lined up to migrate to the electron deficient center (**5-rot**), and the α-*tert*-butyl-α-methylbenzyl cation (**2**), to obtain zero-point energies and free energies at −95 °C. The TSs and ISs had as expected one and zero imaginary frequencies, respectively, except for **5** which had a small imaginary frequency at both the HF/3–21G and HF/6–31G* levels. Thus, **5** does not appear to be an intermediate at the Hartree–Fock (HF) level. Points on the 1,2-phenyl migration PES were determined at the HF/3–21G and the HF/6–31G*-(bonds & angles) levels, while points on the 1,2-methyl migration PES were determined at the HF/3–21G level. All HF/6–31G* IS and TS geometries and the geometries which determine the 1,2-phenyl shift PES at the HF/6–31G*(bonds & angles) level were used to determine MP2, MP3, and MP4(SDQ)/6–31G* correlation energy corrections. The highest level of theory, MP4(SDQ)/6–31G*, indicates that (1) **5-rot** is the least favored intermediate since it is 4.64 kcal/mol higher in energy than the most favored intermediate ion, **2**, at −95 °C; (2) the phenonium ion, **5-TS**, is an intermediate; (3) **5** is not an intermediate; (4) the phenonium ion is only 0.29 kcal/mol less stable than the benzyl cation, **2**, at −95 °C; and (5) the theoretical free energy of activation at −95 °C of 9.34 kcal/mol for the methyl migration is at least 2.4 kcal/mol higher than the actual value in Magic Acid/SO_2ClF which was estimated by Olah et al. using ^{13}C NMR. They determined by proton and ^{13}C NMR that **2** is the predominate ion in superacid and suggested that significant amounts of a partially phenyl-bridged **5** are in equilibrium with **2**. Given that the theoretical PES is correct, it is implied that solvation stabilizes the methyl migration TS more than the benzyl cation and the benzyl cation more than the phenonium ion. Finally, this theoretical study provides excellent calibration for the theoretical study of the larger $C_{19}H_{25}^+$ ion in the region of the 2-*tert*-cumyl-2-adamantyl cation.

Introduction

Our interest in the potential energy surface (PES) of the $C_{12}H_{17}^+$ ion in the 2,3-dimethyl-3-phenyl-2-butyl cation region arose from our wish to study a computationally less demanding system which can model the PES for the $C_{19}H_{25}^+$ ion in the 2-*tert*-cumyl-2-adamantyl cation region.[1] We also hoped to establish a level of molecular orbital theory that is sufficient for obtaining a reasonable answer with the larger $C_{19}H_{25}^+$ system. The experimental study provided by Olah, Spear, and Forsyth[2] provides a sufficient benchmark by which to judge the theoretical computations on the $C_{12}H_{17}^+$ ion. We will review here what those experiments have shown, but we will also provide, in some instances, our own interpretation and discussion of those data.

NMR techniques (^{13}C and ^1H) were used to observe the $C_{12}H_{17}^+$ species, **1**, which were obtained in cold Magic Acid/SO_2ClF by ionizing 2,3-dimethyl-3-phenyl-2-butyl chloride (Figure 1).

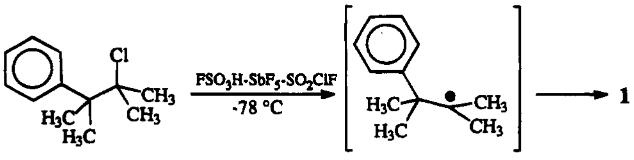
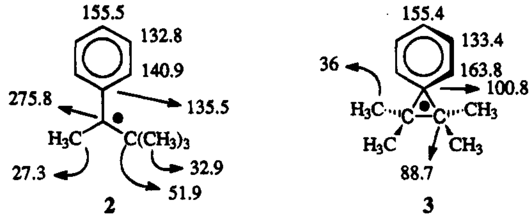


Figure 1. Ionization of 2,3-dimethyl-3-phenyl-2-butyl chloride in Magic Acid/SO_2ClF solution.

Figure 2 shows two possible specific structures for **1**, the α-*tert*-butyl-α-methylbenzyl cation (**2**) and the (tetramethylethylene)benzenium ion (**3**), along with the ^{13}C chemical shifts probably exhibited by them.



2 **3**

Figure 2. Estimated ^{13}C chemical shift values for α-*tert*-butyl-α-methylbenzyl cation (**2**) and the (tetramethylethylene)benzenium ion (**3**).

With one exception, the estimated chemical shifts in Figure 2 follow from known values[2] for the α-ethyl-α-methylbenzyl cation and the ethylenebenzenium ion and standard incremental substituent effects on replacement

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[1] Badejo, I. T.; Choi, H.; Hockensmith, C. M.; Karaman, R.; Pinkerton, A. A.; Fry, J. L. *J. Org. Chem.* **1991**, *56*, 4688–4695.

[2] Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1977**, *99*, 2615–2621.

0022-3263/95/1960-2835$09.00/0

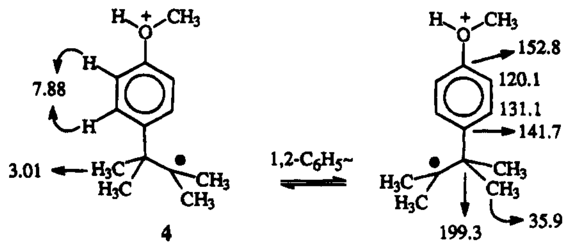

Figure 3. Proton and ^{13}C chemical shift assignments for **4**.

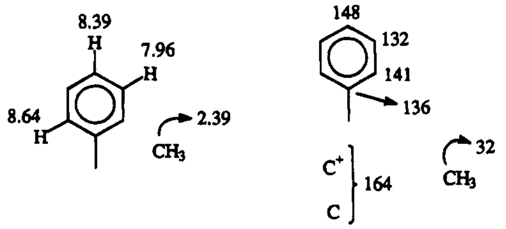

Figure 4. Proton and ^{13}C chemical shift assignments for cation **1**.

of an H atom by a methyl group.[3] The one exception is the chemical shift for the methyl groups of **3** which have no ready analogy. It may be, however, that the methyl groups of **3** resonate at a value similar to that found for the methyl groups of **4**. Cation **4** (Figure 3) consists of rapidly interconverting ions of equal energy in fluoroantimonic acid ($HF-SbF_5$)/SO_2ClF because the protonated methoxy group destabilizes the benzylic ion.[2] Thus, the chemical shifts in Figure 3 are average values for the equilibrium shown. It follows that the resonance values of the methyl groups average to values which might be obtained for a structure midway along the bridging coordinate or a phenonium ion. Cation **4** is also a good model for the alkyl portion of an ideally unbridged 2,3-dimethyl-3-phenyl-2-butyl cation, **5**. The proton and ^{13}C resonances found for **4** thus provide good estimates for those that should be found for **5** since its resonances would also be averaged by rapid 1,2-phenyl shifts.

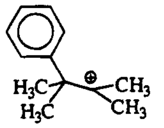

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Figure 4 gives the chemical shift assignments for cationic species **1**. The observed chemical shifts for the unsaturated carbons and the protons attached to them suggest that **1** is mostly composed of the tertiary benzyl cation **2** and argue against **3** as the dominant species. Only one proton and two ^{13}C resonances can be assigned for the four methyl groups and the two carbons bonded to the methyl groups. This is explained by a fast degenerate equilibrium via 1,2-methyl shifts which coalesces the C^+ and quaternary carbon resonances to give an averaged chemical shift at 164 ppm and coalesces the methyl group resonances to give averaged chemical shifts of 32 and 2.39 ppm in the ^{13}C and proton spectra, respectively. Since the estimated values for the C^+ and quaternary ^{13}C resonances of **2**, which are 276 and 52 ppm, respectively, average to the observed value of 164 ppm, the assignment of **1** as being mostly **2** is given strong support. If **1** is mostly an unbridged 2,3-dimethyl-3-phenyl-2-butyl cation (**5**), the average ^{13}C chemical shift for the C^+ and quaternary carbons is expected to be near 199.3 ppm, the value observed for **4**. The resonances for the four methyl ^{13}C atoms of **2** would also resonate at the observed value of 32 ppm if the values estimated for **2** in Figure 2 are averaged together. One obvious anomaly is the lower chemical shift (148 versus 155 ppm for **2**) observed for the para phenyl carbon or C4′ carbon. Olah et al. point out, however, that the indicated decreased charge delocalization into the phenyl ring may be due to nonplanarity in the benzyl cation due to steric interaction between the phenyl and *tert*-butyl groups.[2]

One conclusion derived from the earlier study is problematic. This is that an unsymmetrically phenyl-bridged 2,3-dimethyl-3-phenyl-2-butyl cation (semibridged **5**) is an intermediate which is relatively high in energy yet significantly populated.[2] The intermediacy of semibridged **5** was suggested by the poor fit of the estimated ^{13}C chemical shifts for a fully bridged **3** with the observed NMR resonances and the quenching data for **1**. Addition to methanol at −78 °C gave products mostly derived from a 2,3-dimethyl-3-phenyl-2-butyl cation (79% yield) with the balance derived from **2**. Since **2** rapidly exchanges its methyl groups, it was concluded that semibridged **5** or fully bridged **3**, if they are intermediates rather than saddle points, is present. But neither ion is convincingly evidenced by the NMR data, and the quenching results are not really relevant to the actual structure for **1**.

Finally, another important conclusion from the previous experimental study is the estimate of the activation energy for degenerate interconversion of **2** at −95 °C of 6.9 kcal/mol.[4] This value provides another number for comparison to theory and suggests that intermediate **5-rot** (species with the methyl group aligned for migration to the C^+ center) and, in all likelihood, intermediates **3** and **5** are somewhere within 7 kcal/mol of **2**.

Results and Discussion

Computational Details. Initial geometries were drawn with the interactive molecular-modeling program PCMODEL[5] and then minimized using either PCMODEL or MMX[6] on The University of Toledo's VAX. Geometry optimizations were performed at the semiempirical AM1 level[7] using MOPAC 5.0 and 6.0[8] and at the ab initio HF/3-21G and HF/6-31G* levels using Gaussian 90 and Gaussian 92.[9] In this work, HF/6-31G*(bonds & angles)

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(3) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons: New York, 1982; Chapter 5, p 261.

(4) The number reported earlier[2] appears to have been miscalculated and should be 6.9 not 5 kcal/mol.

(5) Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. In *Advances in Molecular Modeling*; Liotta, D., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 2.

(6) MMX 87.2 and 89.0 source code was kindly provided by J. J. Gajewski and K. E. Gilbert of Indiana University.

(7) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Steward, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(8) *MOPAC*, Version 6.00 and 5.0; Frank J. Seiler Research Laboratory: U.S. Air Force Academy, Colorado Springs, CO, 80840.

(9) (a) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 90*, Revision H; Gaussian, Inc.: Pittsburgh, PA, 1990. (b) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision B; Gaussian, Inc.: Pittsburgh, PA, 1992.

refers to a geometry where, except in the instances where a bridging angle was held constant, all bonds and angles were optimized at the HF/6-31G* level with the dihedral angles held at the values determined by the HF/3-21G geometry optimizations. The transition states (TSs) for the 1,2-methyl shift and the 1,2-phenyl shift were located at the HF/3-21G and HF/6-31G* levels using Opt=(CalcFC,TS); frequency calculations were performed to obtain the imaginary frequency which characterizes each TS. The initial states for the latter two processes were also optimized at the HF/3-21G and HF/6-31G* levels and characterized by their vibrational frequencies. Zero-point energy corrections and free energies were obtained from frequencies scaled by a factor of 0.9. Also, frequencies which were flagged by the Gaussian programs as being too low were replaced with $^1/_2$RT to evaluate the total change in the enthalpy of vibration.[10] Relative free energies were determined at −95 °C by calculating the change in enthalpy of vibration, the entropy of vibration, and the entropy of rotation. MP4(SDQ), MP3, and MP2/6-31G* single-point calculations on the HF/6-31G* and HF/6-31G*(bonds & angles) geometries were performed using the frozen core approximation to obtain the correlation-corrected energies. The AVS Chemistry Viewer on the University of Toledo's Kubota Pacific 3040 graphic supercomputer was useful in assigning **Z** matrices to some ions with the desired symmetry constraints and in adding a dummy atom to the center of the phenyl ring. AM1 calculations as well as some of the ab initio calculations using Gaussian 90 were performed on the 3040 graphic supercomputer. All other ab initio calculations, including all MP4(SDQ)/6-31G* single-point jobs, were performed on the Ohio Supercomputer Center's CRAY Y-MP8/864.

Hartree−Fock $C_{12}H_{17}^+$ PES. Geometries for **2**, **5-rot**, and **5** were obtained by optimizations at the semiempirical AM1 level. The AM1 structures for **2** and **5-rot** were then optimized at the HF/3-21G level with no symmetry constraints. We optimized **5** with no symmetry constraints and then again with local C_s symmetry enforced. These symmetry constraints applied to the phenyl and methyl groups and in effect locked the C2−C3 carbon bond of the 2,3-dimethyl-3-phenyl-2-butyl cation so that no rotation could occur. The phenyl group was not constrained and could rotate so that C_s symmetry for the molecule as a whole could be broken during geometry optimization. Both optimizations produced the same geometry and energy. We probed the phenyl migration PES profile at the 3-21G level by stepping the bridging angle variable (*A9*) down in 5° increments to 65° and optimizing within local C_s symmetry at each step. It was necessary in the latter calculations to use a dummy atom in the **Z** matrix placed at the center of the benzene ring to prevent ring distortion.[11] The minimum energy reaction pathway (MERP) so obtained was well-behaved (Figure 5).

The HF/3-21G structure with a phenyl-bridging angle of 65° was optimized to a transition state (TS) with local C_s symmetry enforced as before. The TS is indicated in Figure 5 at an angle of 66.04° and an energy of 7.92 kcal/mol which is very near the maximum of the potential energy curve. The TS structure, **5-TS**, is essentially of C_{2v} symmetry since the two bridging C−C bonds connected to the bridging phenyl group are 1.757 and 1.758 Å and all methyl groups are equivalent; the C−C bond over which the phenyl migrates is 1.427 Å. As expected, a frequency calculation gave one imaginary frequency equal to 237.1630*i* cm^{-1}.

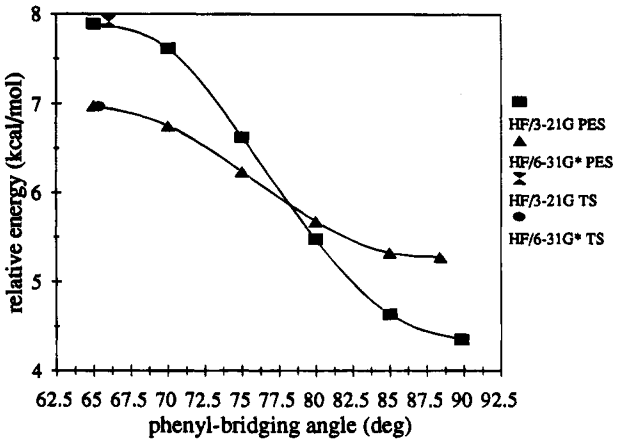

Figure 5. Phenyl migration PES profile at the HF/3-21G//HF/3-21G and HF/6-31G(d)//HF/6-31G*(bonds & angles) levels for the C_s 2,3-dimethyl-3-phenyl-2-butyl cation. Energies are relative to the α-*tert*-butyl-α-phenethyl cation (**2**).

Frequency calculations on **5-rot** and **2** showed them to be ground states with no imaginary frequencies. Curiously, the frequency calculation on **5** revealed a small imaginary frequency of 55.5217*i* cm^{-1}. Since we optimized **5** without symmetry constraints and got a geometry with insignificant deviation from C_s symmetry and the same energy, constraining **5** to local C_s symmetry is not the cause of the imaginary frequency. Therefore, at the HF/3-21G level, **5** is not a true intermediate and has C_s symmetry. The stabilizing interaction of the phenyl group π system with the empty p orbital is clearly indicated by the reduced phenyl−C−C$^+$ angle of 89.83°.

Table 1 contains the absolute energies relative to **2** in units of kilocalories per mole. Hartree−Fock theory at the 3-21G level with no zero-point energy (ZPE) correction clearly favors the benzyl cation **2** since the next most stable isomer is **5** which is 4.35 kcal/mol less stable at 0 °C. Structure **5-rot** is only slightly less stable than **5** at an energy of 4.98 kcal/mol. Species **5-TS** corresponds to the fully bridged phenonium ion and, as noted above, is disfavored by 7.92 kcal/mol.

Addition of ZPE corrections decreases the HF/3-21G energies in Table 1 by about 1 kcal or less to give the values shown in Table 2. The ZPE-corrected relative energies are 3.56, 3.69, and 7.39 kcal/mol for **5**, **5-rot**, and **5-TS**, respectively. Energy corrections for these ions at −95 °C which accounted for the changes in the enthalpy of vibration and the entropies of rotation and vibration gave relative free energies that are shown in Table 2. The latter energy corrections increased the relative energy of **5** and **5-TS** by 0.02 and 0.43 kcal/mol, respectively, to 3.58 and 7.82 kcal/mol. The relative free energy for **5-rot** is 0.44 kcal/mol lower than the ZPE-corrected energy; thus, this ion is the most affected by the energy corrections since it is stabilized by 1.73 kcal/mol in total and becomes more stable than **5**. Structure **5** is stabilized by 0.77 kcal/mol, whereas **5-TS** is stabilized by only 0.1 kcal/mol in total by these corrections.

At the HF/6-31G(d) level of theory, we first optimized only the bond-and-angle variables of the 3-21G structures for **2**, **5-rot**, and **5** to provide as good a comparison as

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[10] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Theory*; John Wiley & Sons: New York, 1986; p 260.

[11] Clark, T. *A Handbook of Computational Chemistry*; Wiley & Sons: New York, 1985; p 184.

Table 1. Energies (kcal/mol) of $C_{12}H_{17}^+$ Ions Relative to the α-*tert*-Butyl-α-phenethyl Cation 2

	level of theory									
			HF/6-31G*		MP2/6-31G*//HF/6-31G*		MP3/6-31G*//HF/6-31G*		MP4(SDQ)/6-31G*//HF/6-31G*	
species[a]	AM1	HF/3-21G	partial	full	partial	full	partial	full	partial	full
5	8.20	4.35	5.28	5.25	0.67	0.02	2.81	2.4	2.33	1.98
5(85)		4.64	5.32		−0.77		1.96		1.58	
5(80)		5.48	5.68		−2.47		0.99		0.81	
5(75)		6.63	6.24	6.16	−3.59		0.38		0.39	
5(70)		7.62	6.76		−4.07		0.14		0.28	
5-TS		7.92		6.82		−4.17		0.05		0.21
5(65)[b]	21.04	7.89	6.98	6.82	−4.08		0.17		0.35	
5-rot	7.91	4.98	6.78	6.71	7.19	7.26	6.98	7.06	6.56	6.59
5-rot(85)	19.37	9.15								
5-rot(70.66)	32.54	14.76	15.30	15.28	7.49		9.68		10.30	
5-rot-TS		14.79		15.37		7.38		9.64		10.29
5-rot(65)	31.33	14.09								
5-rot(55)	21.27	8.78								

[a] For species **5**, the numbers in parentheses denote the methyl−C−C angle in degrees. For species **5-rot**, the numbers in parentheses denote the phenyl−C−C angle in degrees. [b] The AM1 energy is actually for **5(63)**; i.e. the phenyl−C−C angle is 63°. Species **5(63)** lies near a local minimum in the AM1 phenyl migration potential energy profile.

Table 2. Zero-point Corrected and Free Energies at −95 °C (kcal/mol) of $C_{12}H_{17}^+$ Ions Relative to the α-*tert*-Butyl-α-phenethyl Cation 2

	level of theory									
	HF/3-21G		HF/6-31G*		MP2/6-31G*//HF/6-31G*		MP3/6-31G*//HF/6-31G*		MP4(SDQ)/6-31G*//HF/6-31G*	
species	ZPE-corr	ΔG	ZPE-corr	ΔG	ZPE-corr	ΔG	ZPEcorr	ΔG	ZPE-corr	$\delta\Delta G$
5	3.56	3.58	4.46	4.69	−0.77	−0.55	1.64	1.86	1.20	1.42
5-TS	7.39	7.82	6.34	6.90	−4.65	−4.09	−0.43	0.13	−0.27	0.29
5-rot	3.69	3.25	5.30	4.77	5.84	5.31	5.65	5.12	5.17	4.64
5-rot-TS	13.46	13.55	14.14	14.41	6.15	6.43	8.41	8.69	9.06	9.34

possible with the computations done on the $C_{19}H_{25}^+$ ions to be presented in another paper. In addition, we did a HF/6-31G(d) optimization of the bond-and-angle variables of the HF/3-21G structures, **5(85)**, **5(80)**, **5(75)**, **5(70)**, and **5(65)**, found to describe the phenyl-bridging coordinate. These relative energies shown in Table 1 and Figure 5 indicate again that, at the Hartree−Fock (HF) level, the benzyl cation **2** is the most stable and that **5** with a phenyl-bridging angle of 88.39° is the next most stable ion and is 5.28 kcal/mol less stable than **2**. HF theory at the 6-31G* level and experiment both predict that **5** is mostly **2**.

There are some obvious trends apparent in going from the HF/3-21G to the HF/6-31G* level. Figure 5 shows that HF/6-31G* **5** is destabilized relative to HF/3-21G **5**, but the energy differences indicated in Table 1 between the HF/3-21 and HF/6-31G* levels show **5-rot** to be even more destabilized than **5**. Thus, the energy gap between **5** and **5-rot** is larger at the HF/6-31G* level. In addition, the HF/6-31G* phenyl migration PES is much flatter than the HF/3-21G one so that the fully bridged phenonium ion is more stable at the HF/6-31G* level. In other words, addition of polarization functions favors phenyl bridging.

The partially optimized HF/6-31G* structure with a phenyl-bridging angle of 65° was fully optimized with the angle held at 65° and then optimized to a transition state with local C_s symmetry enforced as described above. This TS is indicated in Figure 5 at an angle of 65.35° and is very near the maximum of the potential energy curve. The TS structure, **5-TS**, has C_{2v} symmetry since the two bridging C−C bonds connected to the bridging phenyl group are 1.712 Å and all methyl groups are equivalent; the C−C bond over which the phenyl migrates is 1.428 Å. As expected, a frequency calculation gave one imaginary frequency equal to 123.6359*i* cm^{-1}. Not unexpected either is the decrease in the value of the imaginary frequency found at the HF/3-21G level by ~114*i* cm^{-1} since Figure 5 clearly indicates that the HF/6-31G* phenyl migration PES is relatively flat.

HF/6-31G* frequency calculations were performed on **5** and **5-rot** after all variables were optimized at the HF/6-31G* level. Species **5-rot** was a stable ground state since there were no imaginary frequencies. As found at the HF/3-21G level, **5** has one imaginary frequency, but at the HF/6-31G* level, the value is significantly lower at 12.4270*i* cm^{-1}. Symmetry constraints for all methyl group hydrogen bonds, angles, and dihedrals were removed, and one methyl group attached to the C$^+$ center was rotated 180°. Optimization of the latter structure produced the original structure and the same energy. In addition, this structure also gave a similar value for the imaginary frequency. Thus, at least up to the HF/6-31G* level of Hartree−Fock (HF) theory, **5** is not a true intermediate.

The HF/6-31G* ZPE corrections and the additional corrections to obtain the free energies for **5**, **5-TS**, and **5-rot** are similar to the values found at the HF/3-21G level as can be seen by comparing the values in Tables 1 and 2. Again the largest net effect is on **5-rot** whose energy decreases 1.94 kcal/mol to 4.77 kcal/mol at −95 °C, which is just slightly greater than the relative free energy found for **5** of 4.69 kcal/mol.

As mentioned above, a rough activation energy for the degenerate interconversion of the α-*tert*-butyl-α-methylbenzyl cation of ca. 7 kcal/mol was determined in the earlier experimental study.[2] Thus, we can further test the accuracy of the theoretical method by determining an approximate activation energy for methyl migration in **2**. First, the TS structure for methyl migration, **5-rot-TS**, was determined at the AM1 level using MOPAC 6.0 and the TS keyword.[12] Then **5-rot-TS** was used in an AM1 reaction coordinate study to obtain the minimum energy reaction pathway (MERP) as a function of the

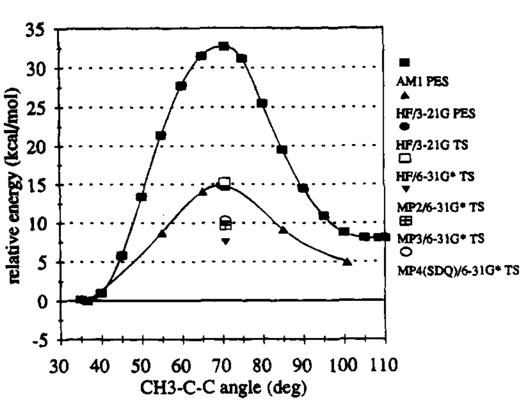

Figure 6. Methyl migration PES profile at the AM1 and HF/3-21G//HF/3-21G levels. Also indicated are the energies for the HF/3-21G and HF/6-31G(d) TS structures and the MP2/6-31G(d), MP3/6-31G(d), and MP4(SDQ)/6-31G(d) energies at the geometry of the HF/6-31G* TS. Energies are relative to the α-*tert*-butyl-α-phenethyl cation (**2**).

CH_3-C-C bond angle to both initial states, **2** and **5-rot**. The AM1 energies obtained for the structures are shown in Figure 6. Figure 6 shows that the AM1 TS is ~26 kcal/mol too high. Overestimation of the 1,2-shift activation energy by the AM1 method is seen also in the large decrease in relative energy for **5(65)** as one proceeds to the HF/3-21G level from the AM1 level in Table 1.

The AM1 structures with CH_3-C-C angles of 55, 65, 70.66, and 85° (**5-rot(55)**, **5-rot(65)**, **5-rot(70.66)**, and **5-rot(85)**, respectively) were used to obtain the HF/3-21G MERP. The structures for **5-rot(55)** and **5-rot(65)** were found to have their phenyl group rotated in a manner which clearly was out of line with the dihedrals for **5-rot(70.66)** and **5-rot(85)**. This is seen also in the somewhat lopsided shape of the AM1 curve. After it was rotated to the correct position, significantly lower energies were obtained. Also, the structure for **5-rot(65)** required a dummy atom in the middle of the phenyl group to constrain it from distorting. The resulting HF/3-21G potential energy profile shown in Figure 6 indicates that the position of the TS has not changed much but that the activation barrier has decreased by 17.41 kcal/mol between the AM1 and HF/3-21G levels. Since we wanted to obtain an accurate activation energy, we felt it worthwhile to reminimize **2**, after rotating the phenyl group to obtain perfect overlap of its π system with the empty p orbital. This required rotation of the *tert*-butyl group to minimize steric repulsion between a *tert*-butyl methyl group and the phenyl group. The latter rotation produced eclipsing of the bonds of the vicinal methyl groups. The latter structure was found to be 2.97 kcal/mol less stable than the original structure and was converted back to the original structure by geometry optimization. Thus, the activation energy for methyl migration at the HF/3-21G level is about 14.76 kcal/mol.

The HF/3-21G structure with a methyl-bridging angle of 70.66° was optimized to a transition state. This TS, **5-rot-TS**, is indicated in Figure 6 at an angle of 69.73° and is very near the maximum of the potential energy curve. The bridging methyl C−C bond connected to the benzylic carbon is 1.908 Å, while the other bridging methyl C−C bond is 1.936 Å; the C−C bond over which the methyl migrates is 1.401 Å. The HF/3-21G frequency calculation gave one imaginary frequency equal to 336.6826*i* cm^{-1}. Thus, the activation energy at 0° is 14.79 kcal/mol. Use of the zero-point-corrected energies decreases the activation energy by 1.33 kcal/mol to 13.46 kcal/mol. The free energy of activation at −95 °C was found to be 0.09 kcal/mol higher at 13.55 kcal/mol.

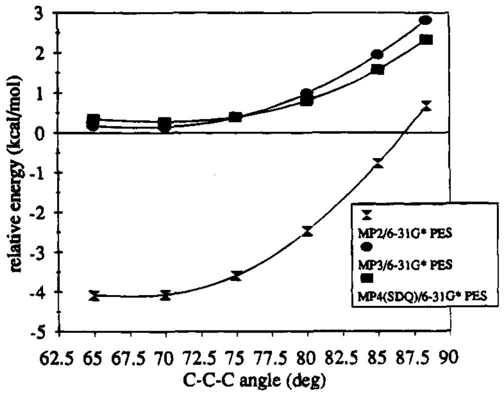

Figure 7. Phenyl migration PES profile at the MP2/6-31G(d), MP3/6-31G(d), and MP4(SDQ)//HF/6-31G*(bonds & angles) levels for the C_s 2,3-dimethyl-3-phenyl-2-butyl cation. Energies are relative to the α-*tert*-butyl-α-phenethyl cation (**2**).

Next, we optimized the bonds and angles of 3-21G **5-rot(70.66)** at the 6-31G* level. The energy relative to **2** increased slightly to 15.30 from 14.76 kcal/mol. Full HF/6-31G* optimization of **5-rot(70.66)** with the methyl-bridging angle held at 70.66° decreased the energy only 0.02 kcal/mol to 15.28 kcal/mol. The latter structure was optimized to a transition state. This TS, **5-rot-TS**, is indicated in Figure 6 at an angle of 68.78°. The bridging methyl C−C bond connected to the benzylic carbon is 1.852 Å, while the other bridging methyl C−C bond is 1.874 Å; the C−C bond over which the methyl migrates is 1.399 Å. The HF/6-31G* frequency calculation gave one imaginary frequency equal to 323.5038*i* cm^{-1}. Thus, the activation energy at 0° is 15.37 kcal/mol. Use of the zero-point-corrected energies decreases the activation energy by 1.23 kcal/mol to 14.14 kcal/mol. The free energy of activation at −95 °C was found to be 0.27 kcal/mol higher at 14.41 kcal/mol. The TS for the 1,2-methyl shift is in marked contrast to the TS for the 1,2-phenyl shift. Addition of polarization functions destabilizes the methyl migration TS by 0.6 kcal/mol but stabilizes the phenyl migration TS by 1.1 kcal/mol relative to the benzyl cation, **2**.

Moller−Plesset Corrections to the Energies. The MP2/6-31G* PES for phenyl migration was determined by MP2/6-31G*//HF/6-31G*(bonds & angles) computations. The phenyl migration PES shown in Figure 7 shows a dramatic change in the PES since the phenonium ion now appears to be a minimum, not a TS, and has become the most stable ion with an energy 4.1 kcal/mol below the benzyl cation **2**. Of course, this deviates by a large amount from the experimental results, which show that the benzyl cation is the most stable ion in the 2,3-dimethyl-3-phenyl-2-butyl cation region of the $C_{12}H_{17}^+$ PES. Significantly, the MP2/6-31G*//HF/6-31G*(bonds & angles) of **5-rot** indicates only a small increase in relative energy of 0.41 kcal/mol over the HF value. The **5**, **5-rot**, **5-TS**, and **5-rot-TS** energies shown in Table 1 from the MP2/6-31G*//HF/6-31G* calculations indicate only small differences from the energies obtained from the bonds-and-angles jobs.

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(12) The initial geometry was obtained from the analogous structure from the AM1 study of the $C_{19}H_{25}^+$ ion in the 2-*tert*-cumyl-2-adamantyl cation region of the PES by simply deleting the extra carbon atoms of the adamantyl ring.

The explanation for the large discrepancy between the theory and experiment is probably the well-known fault of the MP2 correlation correction to overestimate the stability of bridged structures such as the phenonium ion which have stretched C−C bonds.[13] This has been noted recently in a study of the homotropylium cation and the $C_9H_9^+$ PES where it was pointed out that proceeding to the MP3 level and especially the MP4(SDQ) level corrects the problem of artificial stabilization of structures with stretched bonds.[14] In agreement, the computed MP3 phenyl migration PES from MP3/6-31G*//HF/6-31G*-(bonds & angles) calculations shows an increase in energy relative to **2** for all points along the phenyl migration coordinate. It is clear and expected that the MP3 correction is largest for structures with greater bridging character; for example, **5**'s energy is increased by 2.1 kcal/mol, whereas **5(65)**'s energy is increased by 4.25 kcal/mol. Structure **5(65)** is now just slightly *less* stable than the benzyl cation **2** by 0.17 kcal/mol. Again, this change in the level of calculation does not significantly affect the relative energy for **5-rot** since its MP3/6-31G*//HF/6-31G*(bonds & angles) energy decreased by only 0.21 kcal/mol to 6.98 kcal/mol. The **5**, **5-rot**, **5-TS**, and **5-rot-TS** energies shown in Table 1 from the MP3/6-31G*//HF/6-31G* calculations indicate only small differences from energies obtained from the bonds-and-angles jobs. It is noted, however, that the minimum in the MP3 curve in Figure 7 is no longer at 65°. This should not be seen as an indication that the structure is deviating from symmetrical bridging but perhaps as the result of the dihedrals not being optimized. This is corroborated by the MP3/6-31G* energy for **5-TS**, which is lower than the energies for both **9(65)** and **9(70)** and which has a C_{2v} symmetry.

Proceeding to the MP4/6-31G//HF/6-31G*(bonds & angles) level produced only a small effect in the PES that can be seen in Figure 7. The energy of **5(65)** relative to **2** increased to 0.35 kcal/mol at the MP4(SDQ)/6-31G(d) level. Thus, theory appears to be close to the correct theoretical gas phase values. Since experiment indicates **1** to be mostly or all **2**, it is clear that the gas phase energies are overestimating the stability of the bridged ion **3** in Magic Acid solution by at least ~2 kcal/mol but by no more than 7 kcal/mol which is the estimated energy for methyl migration from the benzyl cation **2**. The MP4-(SDQ) relative energy curve for phenyl migration shown in Figure 7 and the MP4(SDQ) energy found for **5-TS** indicate that symmetrically phenyl-bridged **3** is more stable than the semibridged forms of **5**. The latter result is in contrast to the suggestion that semibridged **5** is significantly more stable than **3**.[2]

The HF/6-31G* ZPE corrections and corrections to obtain the relative free energies were added to the MP2, MP3, and MP4(SDQ) energy corrections to give the numbers in Table 2. These corrections are not very important for **5**, **5-rot**, and **5-TS**. For **5** at the MP4-(SDQ)/6-31G* level, the ZPE energy correction makes **5-TS** more stable by 0.27 kcal/mol than **2**, but this effect is largely canceled by the additional energy corrections for −95 °C since the free energy of **5-TS** is 0.29 kcal/mol higher than that for **2**.

The Moller−Plesset single-point calculations showed similar effects on the methyl migration PES for the same reasons. Thus, the MP2/HF6-31G*//HF/6-31G* job on **5-rot-TS** reduced the relative energy by 7.99 kcal/mol to 7.38 kcal/mol. This is similar to, though significantly less than, the reduction in energy for the phenonium ion, **5-TS**, of 10.99 kcal/mol between the same levels of theory. The MP3/6-31G*//HF/6-31G* job increased the relative energy by 2.26 kcal/mol to 9.64 kcal/mol, which is similar to but again less than the increase for **5-TS** of 4.22 kcal/mol. Finally, the MP4(SDQ)/6-31G*//HF/6-31G* job showed a small increase in relative energy of 0.65 kcal/mol to 10.29 kcal/mol which is more than the 0.16 kcal/mol increase found for **5-TS**. The latter value for the activation energy is 3.4 kcal/mol higher than the estimated experimental value of 6.9 kcal/mol. If the ZPE-corrected numbers are used, the theoretical estimated activation energy decreases to 9.06 kcal/mol; the additional energy corrections give a slightly higher free energy of activation of 9.34 kcal/mol. Thus, we find again that a relative gas phase energy is significantly different than the experimental value in Magic Acid solution, but this time the number is too high, not too low as with the phenonium ion case.

Conclusions. Lack of a drastic change in relative energies between the MP3/6-31G* and MP4(SDQ)/6-31G* theoretical levels suggests that the latter level satisfactorily describes the PES. The MP4(SDQ)/6-31G* PES indicates that (1) **5-rot** is the least favored intermediate since it is 4.64 kcal/mol higher in energy than the most favored intermediate ion, **2**, at −95 °C; (2) the phenonium ion, **5-TS**, is an intermediate; (3) **5** is not an intermediate; (4) the phenonium ion is only 0.29 kcal/mol less stable than the benzyl cation, **2**, at −95 °C; and (5) the theoretical free energy of activation energy at −95 °C of 9.34 kcal/mol for the methyl migration is at least 2.4 kcal/mol higher than the actual value in Magic Acid/SO_2ClF which was earlier estimated using ^{13}C NMR.[2] Given that the MP4(SDQ)/6-31G* PES is correct, it is implied that solvation stabilizes the methyl migration TS more than the benzyl cation and the benzyl cation more than the phenonium. At the MP4(SDQ)/6-31G* level of theory, we can estimate that, in Magic Acid/SO_2ClF, the relative stability of the benzyl cation will be underestimated by at least ~2 kcal/mol but by no more than 7 kcal/mol for the $C_{19}H_{25}^+$ PES in the 2-*tert*-cumyl-2-adamantyl cation region.

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