The 1,2-Hydride Shift Barrier in the Phenyl Cation. An *ab initio* Study

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An exceptionally large 1,2-hydride shift barrier, over 40 kcal/mol, is indicated by high-level theoretical calculations for the phenyl cation.

Because of its thermodynamic instability and high reactivity, the phenyl cation (1) is difficult to study in solution.[1,2] In contrast, $C_6H_5^+$ ions are generated readily in the gas phase by electron impact from benzene and numerous precursors.[3] By employing kinetic methods involving tritium decay in multilabelled molecules, Speranza has provided 'the first experimental evidence for a gas-phase automerization of phenylium ion.'[4] The simplest possible mechanism, a 1,2-hydride shift (Scheme 1), was proposed.

This has led to controversy. Dewar has suggested an alternative explanation,[5] but his rationalization is disputed.[4b] Essential to this problem is the height of the 1,2-hydride shift barrier, (1) → (2). Only calculated minimal basis set (STO-3G) and semi-empirical (MINDO/3) values are available;[5–7] while large, these are in poor agreement (77 *vs.* 44 kcal/mol,† respectively). Extensive *ab initio* calculational studies on smaller carbocations[8] have shown that polarization basis sets (d-functions on carbon and p-functions on hydrogen) and corrections for electron correlation are needed to obtain

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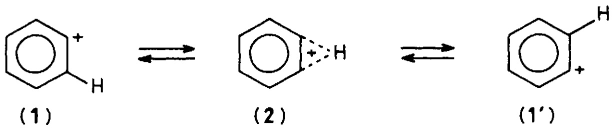
† 1 cal = 4.184 J.



Scheme 1

reliable results. We now report theoretical results at levels which should establish the 1,2-shift barrier with greater certainty.

The geometries of the singlets, (1) and (2), fully optimized with a split-valence basis set (3-21G//3-21G),‡ are shown in Figure 1. We also studied a non-planar protonated form (3), since highly *cis*-bent acetylenes (4) may favour proton attack on the undistorted, perpendicular π cloud,[9] as well as the intriguing pyramidal C_{5v} $C_6H_5^+$ isomer (5)[4,5,7] which has already been examined at 3-21G//3-21G,[10] but not at higher theoretical levels.

Although only (2) is indicated to be a transition structure (one imaginary frequency) at 3-21G, the potential energy surface is very flat for out-of-plane motions of the migrating hydrogen. While no stationary point corresponding to (3) was found at 3-21G, higher level single point calculations actually favoured this form. Thus, we believe the true transition structure for H migration has C_s symmetry [*i.e.*, (3)], but the amount of computer time required precludes a further examination.

At 3-21G//3-21G, (1) is 67.2 kcal/mol more stable than (2). Polarization functions decrease this somewhat, to 63.9 kcal/mol at 6-31G**//3-21G, and electron correlation has a larger effect (52.2 kcal/mol at MP2/6-31G**//3-21G). Further refinements in the theory (not feasible to carry out at present) may lower this value further. The MP2 correction tends to favour bridged structures a bit too much,[8] but geometry optimization at higher levels [especially of (3)] should improve the energy of the transition structure preferentially, so that the final value may be quite near the MINDO/3 estimate.

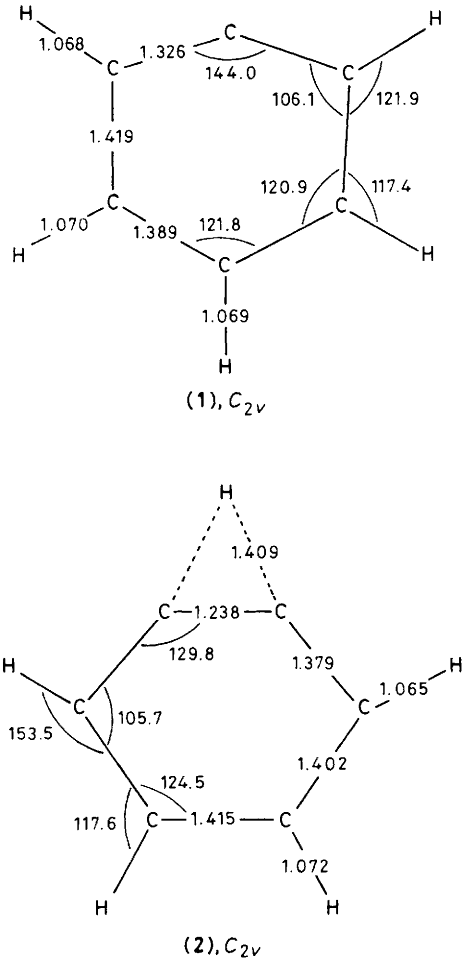
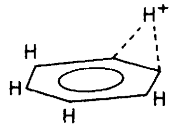
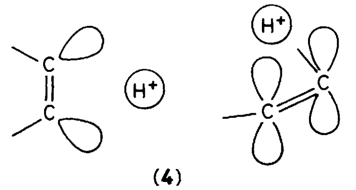


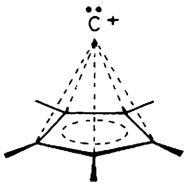
Figure 1. Geometries (3-21G//3-21G) of $C_6H_5^+$ isomers. Bond lengths are in Å, bond angles in degrees.



(3)



(4)



(5)

The pyramidal $C_6H_5^+$ isomer (5) was determined to be a local minimum. Its energy relative to singlet (1) (in kcal/mol) is very sensitive to the theoretical level employed: 25.6 at STO-3G//STO-3G,[6d] 62.0 at 4-31G//STO-3G,[6d] 47.8 at 3-21G//3-21G, 39.8 at 6-31G**//3-21G, and 24.7 at MP2/6-31G**//3-21G. (The MINDO/3 value is 36.7 kcal/mol).[7] However, the (1) → (5) interconversion is formally forbidden and is indicated by MINDO/3 calculations to have a high barrier.[7b] This intermediate (5) can be ruled out by the experimental results[3,4] and other intramolecular pathways involving carbon rearrangements also seem unlikely energetically.[7b,c]

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‡ The notation indicates the level of optimization (after the '//') and the level of single point calculations carried out on these geometries (before the '//'). The Gaussian series of programs with the standard basis sets (3-21G: J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **107**, 939; 6-31G**: P. C. Hariharan and J. A. Pople, *Mol. Phys.*, 1974, **37**, 209) and MP2 electron correlation corrections (C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **44**, 618; J. S. Binkley and J. A. Pople, *Int. J. Quantum Chem.*, 1975, **9**, 229) were employed. *E.g.*, Gaussian 80 (J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, *Quantum Chemistry Program Exchange*, 1981, **13**, 406) was modified for use on a CRAY-1 computer. The absolute energies for (1), (2), and (5), respectively, are −228.46446, −228.35730, and −228.38835, at 3-21G//3-21G; −229.76715, −229.66538, and −229.70365 at HF/6-31G**//3-21G; and −230.52723, −230.44399, and −230.48783 a.u. at MP2/6-31G**//3-21G. The absolute energies of benzene and of the phenyl cation calculated using the 3-21G benzene geometry are respectively, −230.71378; −229.71640 (HF/6-31G**) and −231.50413; −230.47573 a.u. (MP2/6-31G**). Using the energy of the isodesmic reaction, $CH_3^+ + C_6H_6 \rightarrow CH_4 + C_6H_5^+$ (−25.8 kcal/mol at MP2/6-31G**//3-21G) and experimental heats of formation of the other species, ΔH_f° $(C_6H_5^+)$ = 273 kcal/mol is estimated. This is in excellent agreement with the latest experimental values (ref. 3 and S. T. Pratt and W. A. Chupka, *Chem. Phys.*, 1981, **62**, 153).

We conclude that the 1,2-hydride shift barrier in the phenyl cation should be 40 kcal/mol or more. This value is exceptionally large, and is rivalled only in experimentally investigated systems by the barrier separating the 1- and 2-adamantyl cations.[11] In these rigid cage molecules, the vacant carbocation orbital is *orthogonal* to the adjacent C–H bond; unmeasurably high barriers result. In (**1**), the adjacent C–H bonds lie in the same plane as the carbocation orbital, but these are 'splayed out' away from each other. The situation is depicted in (**4**). This leads to poor three-centre overlap in the transition structure (**2**), and an increased barrier. The bridging hydrogen C–H distances in (**2**), 1.409 Å, are considerably longer than those calculated (1.159 Å) for the bridged vinyl cation at 3-21G.[8,12]

Tritium decay[4] should generate a phenyl cation with excess energy. Thus, $C_6H_5^+$, calculated at the 3-21G benzene geometry, is 31.8 and 32.3 kcal/mol (HF/6-31G** and MP2/6-31G**, respectively) less stable than fully optimized (**1**). (The MINDO/3 value is 23.2 kcal/mol using the MINDO/3 benzene geometry for the phenyl cation.) Thus, a vertical decay process should provide much of the energy needed to overcome the 1,2-automerization barrier. However, if such mechanisms are utilized, as suggested by Speranza,[4] additional excess energy must be present.

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