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RING SIZE EFFECTS ON 1,2-SHIFTS IN CARBOCATIONS

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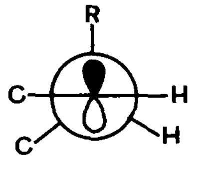
Abstract: 1,2-Hydride shift barriers in classical carbenium ions increase with decreasing ring size; this can be attributed to the increased strain of the H bridged structures in the small rings.

1,2-Shifts in carbenium ions usually are facile processes.[1] However, experimental evidence indicates that higher barriers can be encountered in cyclic systems. For example, 1,2-methyl shifts in cyclopentyl cations require about 1.5 kcal/mole more activation energy than those in acyclic systems.[2] This difference has been rationalized on the basis of orbital orientation.[2] To have a low barrier, the empty p orbital on the cationic center should have a zero dihedral angle with the C-R bond, R being the migrating group. Additional energy is required to achieve this orientation in cyclopentyl cations (compare 1 and 2).



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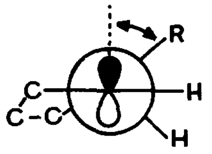

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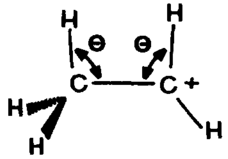

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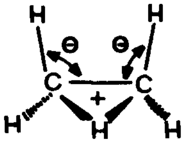

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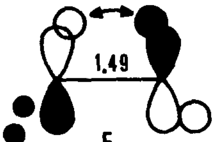
This dihedral angle effect does not explain the even larger 1,2-shift barriers indicated in three and four membered rings and in bicyclic systems,[3-8] but the possibility of nonclassical stabilization due to carbon bridging complicates the interpretation.[9] Using semiempirical and ab initio calculations, we now establish the generality of this ring size effect and explain its origin.

STO-3G[10] calculations were first performed on the ethyl cation, the simplest model system. The energy difference between the classical (3) and bridged (4) structures reflect the height of the barrier to hydride shift. We are not concerned here with the absolute accuracy of the calculated differences, but rather with the trend as the geometry is altered. To simulate ring systems, the two vicinal HCC angles, θ in 3 and 4, were fixed at different values while maintaining the other parameters at their original values. As indicated by the data in Table 1, the calculated energy differences (barriers) increase with decreasing θ monotonically. Thus, the ring size effect should be a general phenomenon and is not due to exceptional behavior of a specific carbenium ion.

This effect can be explained in classical terms. The optimized value of θ for the bridged cation, **4**, is 120.6°, while the HCC angle θ at the methyl group in the classical structure, **3**, is much smaller (112.9°).[11] Therefore, incorporation of **4** into a small ring leads to greater angle strain. The shorter C-C distance in **4** (1.403 vs. 1.488Å in **3**)[11] also contributes to the effect. Orbitals **5** and **6** suffer the most destabilization in **3** and **4**, respectively, during <HCC reduction. There is considerable H-H repulsive character in these orbitals at small HCC angles. But for a given HCC angle, the repulsion in **5** is much smaller due to the larger C-C distance in **3**. A strong preference for the classical structure results.



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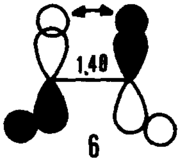

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Hydride shifts in the 2-butyl cation and in 3,4, and 5 membered rings were then calculated (MINDO/13[12] and STO-3G). All geometries were completely optimized using the Davidon-Fletcher-Powell method with the indicated symmetry constraints (Table 2). Note the planar structures for the classical cations.[9] The resulting MINDO/3 and STO-3G classical-bridged energy differences (Table 3, columns 2 and 4) do not agree in absolute values, but this reflects the fault of STO-3G to favor open over bridged structures;[13] the MINDO/3 results are close to those obtained with large basis set *ab initio* calculations with inclusion of electron correlation.[14] However, if these energy differences (Δvalues) are set relative to those of ethyl (Table 3, columns 3 and 5), the same trends are shown by the MINDO/3 and the STO-3G results. The ring size effect is seen clearly. The calculated 1,2-H shift barriers increase along the series: 2-butyl<cyclopentyl<cyclobutyl<cyclopropyl.

The available experimental results (Table 3) in stable ion solutions are not directly comparable to the calculations which refer to the gas phase. Some of the experimental systems involve carbon-bridged ions, not considered in our calculations.[9] Nevertheless, the same trend towards increasing barriers with decreasing ring size is apparent. 1,2-Hydride shifts in cyclobutyl cations have been detected only recently; barriers significantly greater than those in five membered rings are found.[4] The much larger predicted barrier in the cyclopropyl cation is also consistent with the failure of deliberate attempts[5] to observe 1,2-shifts in a variety of cyclopropyl systems prior to rearrangement to allyl cations. The barrier to *exo*-3,2-hydride shift in the 2,3-dimethyl-2-norbornyl cation[6] is 3.5 kcal/mole higher than that in the 2,3-dimethyl-2-butyl cation (3.1 kcal/mole).[3] The much larger 3,2-shift barrier in the parent 2-norbornyl cation (>10.8 kcal/mole)[7] indicates its nonclassical character;[14] 1,2-H shifts in classical secondary cation systems have *lower* barriers than their tertiary counterparts (Table 3). In the bicyclo[2.1.1]hexyl cation, at least part of the even higher barrier to 3,2-hydride shift (>13 kcal/mole)[8] must be attributed to the ring size effect.

Table 1. STO-3G Energies (in Hartrees) of Distorted Ethyl Cations

θ	Classical 3	Bridged 4	Difference, kcal/mole
Opt.	-77.40770[a]	-77.38986[a]	11.2
109.5°	-77.40001	-77.37921	13.1
90°	-77.32928	-77.29250	23.1
70°	-77.06935	-77.97198	61.1

[a] Fully optimized structures (ref.11).

Table 2. MINDO/3 Heats of Formation (kcal/mole) and STO-3G Energies (Hartrees) of Classical and Hydride Bridged Cations

Ion	Symmetry	ΔH_f^{o}, MINDO/3	E, STO-3G
Ethyl, classical, bisected	C_s	213.7	-77.40806[a]
Ethyl, H bridged	C_{2v}	205.7	-77.38986[a]
2-Butyl, classical, trans	C_s	175.7[b]	-154.61199[b]
2-Butyl, H bridged, trans	C_2	170.6[b]	-154.59024[b]
Cyclopentyl, classical	C_{2v}	183.1[c]	-192.04186
Cyclopentyl, H bridged	C_s	182.4	-192.01872
Cyclobutyl, classical	C_{2v}	210.6[c]	-153.40896[d]
Cyclobutyl, H bridged	C_s	212.8	-153.37824
Cyclopropyl, classical	C_{2v}	237.7[c]	-114.76523[e]
Cyclopropyl, H bridged	C_s	245.0[b]	-114.71166[b]

[a] Ref. 11. [b] Ref. 14. [c] Ref. 15. [d] Ref. 16. [e] Ref. 17.

Table 3. Calculated Energy Differences Between Classical and H Bridged Isomers (Δ) and Experimental Barriers to 1,2-Hydride Shifts (kcal/mole)

System	MINDO/3		STO-3G		Exper. barriers	
	Δ	Rel.Δ	Δ	Rel.Δ	Secondary	Tertiary[a]
Ethyl	-8.0	0.0	11.4	0.0	-	-
2-Butyl	-5.1	2.9	13.7	2.3	<2.5[b]	3.1[b]
Cyclopentyl	-0.7	7.3	14.5	3.1	low	3.1[b]
Cyclobutyl	2.2	10.2	19.3	7.9	(>10)[c,d]	(8.7)[d,e]
Cyclopropyl	7.3	15.3	33.6	22.2	not observed[f]	
2-Norbornyl	4.6[g]	12.6	20.8[g]	9.4	(>10.8)[d,h]	(6.6)[d,i]

[a] H-shift barriers in dimethyl substituted systems. [b] Ref. 3. [c] Ref. 4a. [d] See ref. 9. [e] Ref. 4b. [f] Ref. 5. [g] Ref. 14. [h] Ref. 7. [i] Ref. 6.

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