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CONFORMATIONAL ANALYSIS OF TERTIARY CYCLOALKYL (C_6,C_7,C_8) CARBOCATIONS USING MOLECULAR MECHANICS. COMPARISON WITH STABLE ION EXPERIMENTAL DATA

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Summary. Conformational calculations of the 1-methylcyclohexyl, 1-methylcycloheptyl, and 1-methylcyclooctyl cations agree with reported experimental observations.

Molecular mechanical methods have been widely used to calculate structures and energies of organic molecules.[1] With few exceptions, the calculations have given excellent correlation with experimental information. A lack of experimental structural information on carbocations, however, has slowed the extension of the molecular mechanics method to these transient species.

Despite this difficulty, Schleyer and his colleagues have developed a carbocation force field and have used it to predict solvolysis rates.[2-4] Schleyer reasoned that, ideally, the variation in solvolysis rates can be assessed by evaluating the change in strain that occurs on going from the ground state to the solvolytic transition state. Using the parent hydrocarbon to simulate the ground state and the carbocation to simulate the transition state Schelyer *et. al*. were successful in correlating strain relief with rates of solvolysis for a series of sixteen bridgehead systems[3] and in 2-alkyl-2-adamantyl *p*-nitrobenzoates[4]. In both cases the hydrocarbons and cations are conformationally rigid. We achieved good success in correlating calculated carbocation bond angles with ketone carbonyl infrared absorptions in a rigid polycyclic series.[5] We have also found that the high change in strain between methylcyclooctane and the secondary cyclooctyl cation was consistent with other mechanistic indicators for a strain-induced solvolysis of secondary cyclooctyl derivatives.[6]

Kirchen and Sorensen[7] (KS) have recently reported their conformational analysis of the methyl-substituted tertiary cyclohexyl, cycloheptyl, and cyclooctyl cations using experimental data from the low temperature ^{13}C NMR spectra of the stable ions. These workers found that incorporating an sp2 hybridized center into a ring system led to some interesting differences from the conformational ordering observed for hydrocarbons. For example, the twist-boat form of the cyclohexyl cation was found to be slightly more stable than the chair form. For our own purposes, the availability of experimental conformational information on carbocations provides an opportunity to further assess the accuracy of the Schleyer carbocation force field. Since there is little difference in energy between these conformers, this test is indeed a rigorous one

We have calculated the strain energies of various conformations of the methyl-substituted tertiary cyclohexyl, cycloheptyl, and cyclooctyl cations. The relative strain energies calculated for these ions are shown, along with some experimental data on the cations, in Table I. Since the cycloalkanone series may model cation behavior, Allinger's calculations[8] for the respective ketone conformations are included in the table for comparison.

For the 1-methylcyclohexyl cation, KS found the twist-boat (TB) conformer 2 to be more stable than the chair conformation 1 by 0.5 kcal/mole. Our calculations[9] are in close agreement


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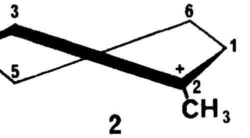

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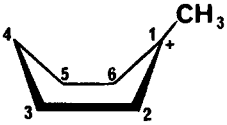

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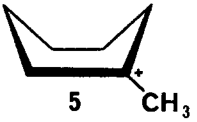

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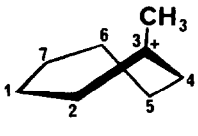
with the KS results, indicating that the chair cation 1 is more stable than 2 by 0.15 kcal/mole. For the respective hydrocarbons, the force field is known to slightly favor the chair form over the TB form (by 0.3 kcal/mole);[1e] correcting for this error leads to the prediction that the TB is slightly the more stable (by 0.16 kcal/mole). It is gratifying to observe that of the two possible TB conformations, i.e., 2 and 3, the one predicted to have lowest energy (i.e., 2)is the conformation suggested by KS to be the more stable. The cyclohexanone calculations of Allinger[8] parallel the cation series.

The 1-methylcycloheptyl cation was described as KS as a "fluxionally mobile molecule." Our calculations of the cation conformations 6-9 suggest that this should be so. In fact, the



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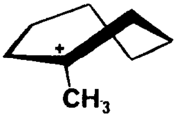

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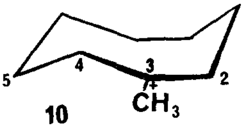
Table 1. Relative Energies of Various Conformations Calculated for the 1-Methylcyclohexyl, Heptyl, and Octyl Cations and the Respective Ketones.

Cation Number	Descriptive Name of Conformation[a]	Calculated Relative Strain Energy in kcal/mole[9]	Calculated Relative Strain Energy of Corresponding Ketone[8]	Experimental Cation Relative Stabilities[7]
1	Chair	0.00	0.00	$\Delta G^{\neq}_{1\to 2} \leq 6$ kcal/mole (-130°C)
2	Twist-Boat (C2+)	0.14	----	
3	Twist-Boat (C1+)	3.24	2.72	
4	Boat (C1+)	13.00	5.33	$\Delta H_{1\to 2} \cong 0.5$ kcal.
5	Boat (C2+)	15.9	----	
6	Twist-Boat-Chair(C3+)	0.00	0.00	"fluxionally mobile"
7	Twist-Boat-Chair(C4+)	0.82	0.25	
8	Twist-Boat-Chair(C2+)	1.29	1.80	
9	Twist-Boat-Chair(C1+)	2.04	1.62	
10	Boat-Chair (C3+)	0.00	0.00	$\Delta G^{\neq}_{10\to ?} = 7.2$ kcal/mole (-105°C)
11	Twist-Crown	0.32	1.46	
12	Boat-Chair (C2+)	6.00	1.71	10 frozen out at -120°C

[a] The designation after some of the descriptions (e.g., C2+, etc.) describes the carbon bearing the charge in our numbered structures. The numbering is solely for convenience in computing.

similar energies for 6-8 suggest that KS observed a mixture of these conformers. Again, simulation of the cations by the ketones gives a similar result except that, for an unknown reason, the stability order of the two higher energy TB forms is reversed in the two calculations.

KS found that a single conformation of the 1-methylcyclooctyl cation was frozen out at -120°C and assigned structure 10 to this conformation. Our calculations predict that the boat-chair[10] conformer 10 is more stable than 11 by only 0.32 kcal/mole. The ketone models, however, do predict a larger margin for 10 over 11. As with the six-membered ring system, Schleyer's hydrocarbon calculations[1e] show that the force field underestimates the stability of the boat-chair form by 1 kcal or more. Thus, if one assumes that the same error is present in the cations, the boat



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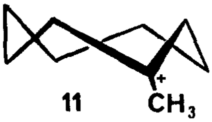

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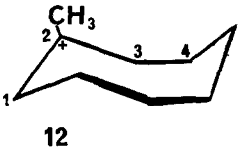

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chair conformer 10 is predicted to be much more stable than 11 and hence follows the experimental observation.

We conclude that the Schleyer force field shows a good ability to predict energy differences between possible conformations of non-rigid cyclic tertiary alkyl carbocations in most cases. Indeed, despite changes in order of stability between the chair and TB forms as one goes from the hydrocarbons to the cations in six-membered rings, the force field accurately follows the trend. These results, in conjunction with earlier successful predictions of solvolysis rates[3-5] and the correlation of calculated carbocation bond angles with ketone carbonyl infrared absorptions,[5] lend credibility to the Schleyer force field for calculation of carbocation structures and energie We are continuing to explore the use of the molecular mechanical method for calculation of carbocation structures.

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9. All structures are energy-minimized beginning with a structure which has bond angles and lengths which approximate the desired conformation. Calculations were performed on a UNIVAC 1100-10 computer using the Schleyer force field[2] for cations.

10. The flexibility of this conformer led to false minimas.[1e] Three different trial geometries were minimized to give final geometries with C2345 dihedral angles and strain energies (kcal/mole) of, respectively: -56.3°, 10.45; -47.7°, 8.14; -44.2°, 8.62.

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