Hyperconjugation in Strained Bridgehead Cyclobutyl Cations: an *Ab initio* Study of Bicyclo[1.1.1]pent-1-yl Cubyl and Norcubyl Cations

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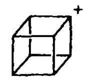
Ab initio molecular orbital calculations (MP2/6-31G**) provide strong evidence that the bicyclo[1.1.1]pent-1-yl, cubyl and tricyclo[3.1.1.0^{3,6}]hept-6-yl (6-norcubyl) cations are principally stabilized by hyperconjugative interaction of the strained α–β and β–γ carbon–carbon bonds with the (vacant) cationic p-orbital; the degree of interaction is strongly dependent on the geometry of the charged four-membered ring in each case.

The stabilities of the cubyl **1** and bicyclo[1.1.1]pent-1-yl **2** cations, as gauged by the relative ease in which appropriate precursors undergo solvolysis, are somewhat enigmatic. For example, cubyl triflate **3** solvolyses with a rate constant 1.7 × 10^{-10} times that of *tert*-butyl triflate,[1] while bicyclo[1.1.1]-pentyl bromide **4** reacts about three times faster than *tert*-butyl bromide under similar conditions.[2] While the solvolytic rate for cubyl triflate **3** appears to be enormously depressed, molecular mechanics calculations predict that **3** and **4** solvolyse 10^{15} and 10^9 times faster, respectively, than expected on the basis of the strain engendered in the formation of the incipient cations in each case.[3]

Recently, we reported that fluorodeiodination of bridgehead iodides by xenon difluoride in dichloromethane provides an excellent procedure for the preparation of bridgehead fluorides.[4] In some instances, however, the product fluoride was contaminated with significant quantities of the corresponding chloride derived by abstraction of chloride from the solvent by the incipient cation. For example, cubyl iodide **5** gave a mixture of the corresponding chloride and fluoride in a ratio of 6 : 94, while 1-iodonorbornane **6**, which solvolyses several orders of magnitude slower than **3**, gave a 25 : 75 ratio of chloride to fluoride. Considering the highly energetic nature of the 1-norbornyl cation it was suggested that the chloride : fluoride ratio is representative of the reactivity (and hence indiscriminate nature) of the cation in each case. Interestingly, 6-iodotricyclo[3.1.1.0^{3,6}]heptane **7** (6-iodonorcubane) gave a 28 : 72 ratio of chloride to fluoride, and on this basis it would seem that the 6-norcubyl ion **8** is substantially more reactive and consequently less stable than the cubyl cation **1**.



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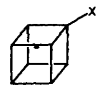
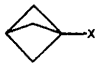
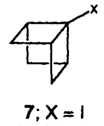


3; X = OSO$_2$CF$_3$
5; X = I
9; X = H

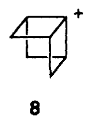


4; X = Cl, Br
10; X = H

6



7; X = I
11; X = H



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Why should systems in which the cationic centre is substantially deviated from planarity be formed under solvolytic conditions at all? Furthermore, why should two apparently similar ions (**1**, **8**) demonstrate significantly different reactivities under identical conditions? Unfortunately, a direct comparison of the two cations **1** and **8** produced under solvolysis conditions is not possible because a solvolytic study of norcubane bearing a suitable leaving group at C(6) has not been reported.

In order to provide an answer to these questions, we sought recourse to high-level *ab initio* (MP2/6-31G**) molecular orbital calculations on the cations **1**, **2** and **8**. Geometries of the cations (**1**, **2**, **8**) and parent hydrocarbons (**9**, **10**, **11**) were fully optimized with the inclusion of electron correlation at the MP2/6-31G** *ab initio* level of theory using standard gradient

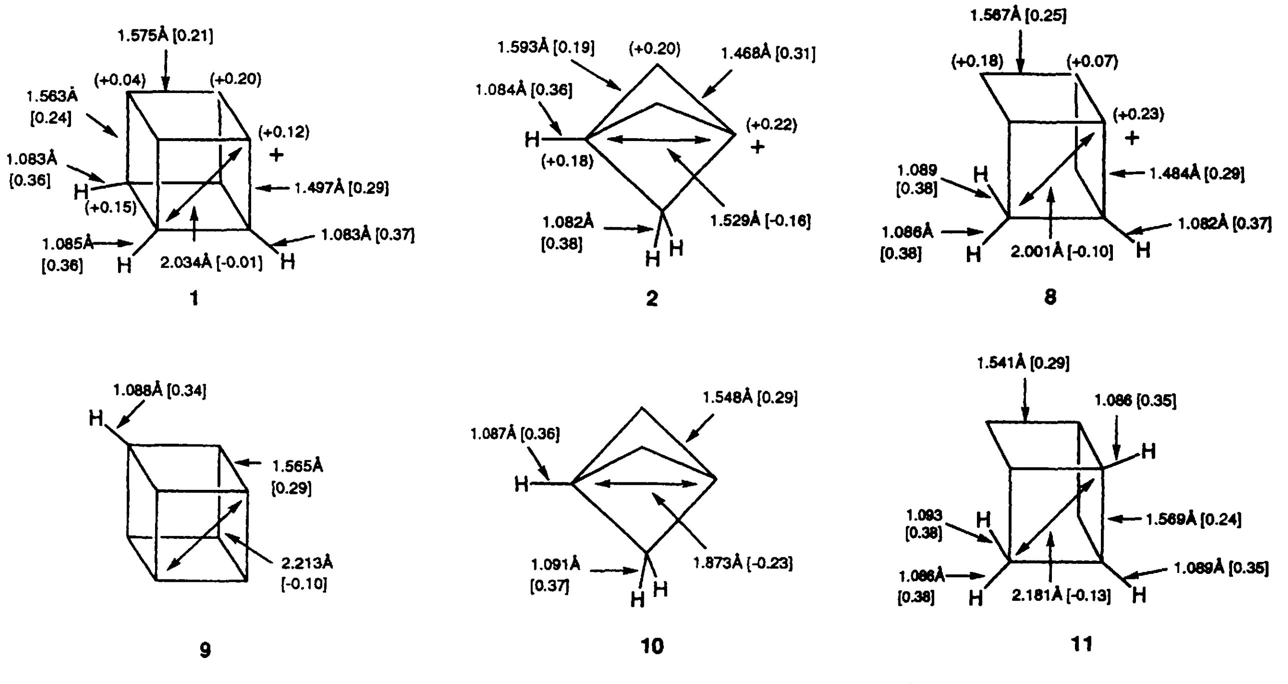
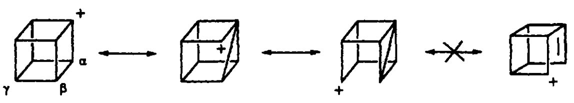


Fig. 1 *Ab initio* results; distances, charges (parentheses) and bond populations [square parentheses]

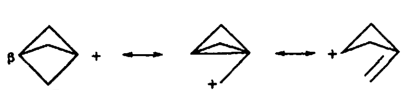
minimization techniques[5] within the Gaussian 92 system of programs.[6] Mulliken population analyses were performed on the MP2/6-31G**-calculated wavefunction in each case. The calculated data are displayed in Fig. 1.

The calculated differences in energy between the cation and the parent hydrocarbon ($RH \rightarrow R^+$) in each case relative to the same difference for the cubyl system (**9** → **1**) are listed in Table 1 and reveal that in agreement with the available experimental data, the bicyclo[1.1.1]pentyl cation **2** is substantially more easily formed from the parent hydrocarbon than is the cubyl cation **1**, while the 6-norcubyl cation **8** is substantially less easily formed; the former cation is predicted to be 39.9 kJ mol^{-1} more stable than **1** relative to the parent hydrocarbon, while the latter is calculated to be 50.6 kJ mol^{-1} less stable.

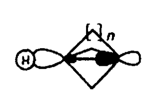
The data presented in Fig. 1 provide insight into why these apparently similar cations display significantly different stabilities. The MP2/6-31G**-calculated geometries, charge distribution and Mulliken population analysis of cubyl cation **1** and cubane **9** indicate that apart from the expected shortening of the C(1)–C(α) bonds (1.497 Å) in **1**, the remaining C–C bonds, at 1.575 Å (α–β) and 1.563 Å (β–γ) show little deviation from that calculated in **9** (1.565 Å). Similar trends were observed by Borden at the RHF/3-21G level of theory.[7] The MP2/6-31G**-calculated (Mulliken) charge distribution in **1** reveals a charge of +0.12 at the formal cationic centre, with extensive charge delocalization to the α-CH groups (+0.20) and γ-CH groups (+0.15) with very little buildup of charge at the β-CH groups (+0.04). In addition, the Mulliken population analysis on the MP2/6-31G**-calculated wavefunction in each case reveals that the C(1)–C(α) bonds in cubyl cation **1** has identical population to that in cubane (0.29). Decreases in the α–β (0.21) and β–γ (0.24) bond populations when compared with cubane are also predicted. The C–H bonds show the expected shortening due to rehybridization, while all C–H bond populations are virtually identical in both species, indicating that the C–H bonds do not become involved in hyperconjugative delocalization. In addition, a substantial decrease in antibonding interaction between C(1) and the β-carbons in **1** (−0.01) when compared with cubane (−0.10) is predicted. These data are consistent with major contributions from resonance structures **12** and **13** to the overall structure of **1**, with little contribution from canonical structure **14**. Eaton had suggested previously a similar stabilizing mechanism to be operating in the cubyl cation **1**.[1,3,8]



1 **12** **13** **14**



2 **15** **16**



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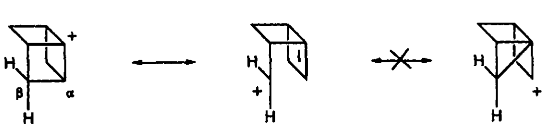


8 **17** **18**

In a similar manner, the calculated data for the bicyclo[1.1.1]pentyl cation **2** and the 6-norcubyl cation **8** predict that canonical structures **15–16** and **17** are important contributors to the overall structure of **2** and **8**, respectively. Significantly, it would appear that **18** is unimportant in stabilizing the 6-norcubyl cation **8**. Additionally, the calculated data provide no evidence for the involvement of C–H hyperconjugation in these cations.

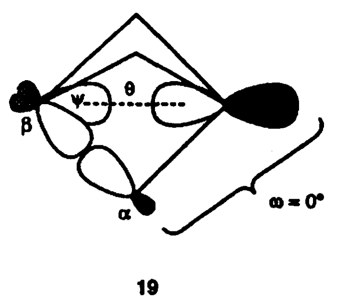
In molecular orbital terms, resonance structures **12–18** represent the symmetric linear combination (ψ) of the strained α–β, and where appropriate, the β–γ C–C bonds which are delocalized towards the cationic (empty) p-orbital in each case. As structure **19** depicts, the interorbital angle of 180° is ideal for this stabilizing mechanism in the bicyclo[1.1.1]pentyl cation **2**. Furthermore, the α–β bonds, which are co-planar (ω = 0°) with the vacant p-orbital, are ideally set up for the p-type interaction represented in resonance structure **16**. It is not surprising, therefore, that **2** is well represented by **15** and **16**.

The picture is somewhat different in the cubyl and norcubyl systems. In the former, canonical structures **12** and **13** are representative of the symmetric linear combination of the α–β and β–γ C–C bonds. The resultant orbital (ψ) subtends an angle (θ) of 110° with the vacant p-orbital, as depicted in **20**, and is sufficient for extensive stabilization. The twist angle (ω) of 45° is not conducive to substantial π-type interaction; as a consequence, the cubyl cation is best represented by resonance structures **12** and **13** with minimal contribution from **14**. Structure **18** represents the linear combination of the α–β bonds at the β-positions in the norcubyl ion **8**. Unlike the cubyl cation, **8** does not contain a suitable β–γ C–C bond and, as **8** is inherently rigid and unable to attain a 'puckered' conformation, the linear combination (ψ) is unable to provide sufficient overlap to stabilize the cationic centre, as depicted in **21**,

Table 1. MP2/6-31G**-calculated energies of the cations (R^+) and parent hydrocarbons (RH) in this study

Structure	E^a	$E(R^+) - E(RH)^b$
1	−307.57142	0.0
9	−308.47912	—
2	−193.73089	−39.9
10	−194.62339	—
8	−270.86472	50.6
11	−271.79172	—

[a] Energy in hartrees (1 H = 2625.5 kJ mol^{-1}). [b] Relative to $E(\mathbf{1})$–$E(\mathbf{9})$; energy in kJ mol^{-1}.



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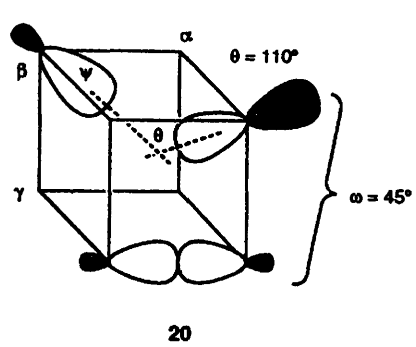

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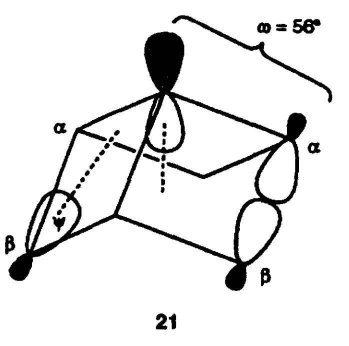

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highlighting the relative unimportance of **18** to the overall representation of the norcubyl ion. The only hyperconjugative stabilizing process available to **8** would as a result appear to involve π-overlap of the type depicted in resonance structure **17**; the twist angle (ω) of 56° suggests that stabilization of this type is minimal. It is no surprise, therefore, that **8** is a high-energy species.

In summary, MP2/6-31G** calculations provide strong evidence that cations **1**, **2** and **8** are principally stabilized by the hyperconjugative interaction of the strained α–β and β–γ bonds with the vacant (cationic) p-orbital in each system. The degree of interaction is strongly dependent on the geometry of the charged four-membered ring in each case. Our previous suggestion[9] that the stabilizing mechanism operating in bicyclo[*n*.1.1]alkyl cations **22** involves the overlap of the vacant p-orbital with the rear-lobe of the cross-ring C–H σ-bond (σ-hyperconjugation) needs to be reviewed in light of these calculational data.

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