7876 *J. Org. Chem.* **1993**, *58*, 7876-7882

Toward an Understanding of the Cubyl and Related Caged Carbocations

Ernest W. Della,*[1] Nicholas J. Head,[1] Wit K. Janowski,[1] and Carl H. Schiesser*[2]

School of Physical Sciences, Flinders University, GPO Box 2100, Adelaide, South Australia, 5001, and School of Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia

Received July 6, 1993•

The product ratios observed upon fluorodeiodination of a series of caged cyclobutane-containing iodides are explained on the basis of the relative energies of the intermediate cations involved. The relative energies of these cations have been evaluated by *ab initio* calculations with the inclusion of electron correlation (MP2/6-31G*//RHF/3-21G; MP2/6-31G**), the results of which lend support to the view that hyperconjugative involvement of the cationic center with the α,β and β,γ C–C bonds in each cyclobutyl moiety is the critical factor responsible for the stability of the cation in each case. The degree of stabilization of the cations is a reflection of the number and relative importance of several resonance contributors (corresponding to the involvement of the carbon σ-framework) to their overall structure and is strongly dependent on the geometry of the rigid carbon framework in each case.

Introduction

We reported recently that fluorodeiodination of a series of bridgehead iodides by xenon difluoride in methylene chloride represents an excellent procedure for the synthesis of bridgehead fluorides.[3] While in most cases the conversion proceeded satisfactorily and gave the fluoride cleanly, it was observed that in two of the systems under investigation the product was contaminated with variable amounts of the corresponding chloride. Thus, whereas 1-iodoadamantane (**1**), 1-iodobicyclo[2.2.2]octane (**2**), and 1-iodobicyclo[3.2.1]octane (**3**) yielded the respective fluorides **4–6** without any detectable quantities of the related chloride, 1-iodobicyclo[2.2.1]heptane (**7**) and iodocubane (**8**) gave bridgehead fluoride/chloride mixtures of 75:25 (**9**, **11**) and 94:6 (**10**, **12**), respectively.

Scheme I

$$RI + XeF_2 \longrightarrow RIF_2 + Xe$$

$$RIF_2 \longrightarrow R^+ + IF_2^-$$

$$IF_2^- \longrightarrow IF + F^-$$

$$R^+ + F^- \longrightarrow RF$$

Evidence was presented to support the intermediacy of bridgehead carbocations in these fluorodeiodination processes (Scheme I), and the production of chlorine-containing products was ascribed to interception of the intermediate cations by solvent. It is noteworthy that the chloride contaminants are produced particularly from those systems in which the bridgehead cations are of relatively high energy; both cubyl triflate (**14**)[4] and 1-bicyclo[2.2.1]heptyl triflate (**13**)[5] for example have been shown to possess very slow rates of solvolysis. If one accepts the reasonable correlation that these high-energy cations are also extremely reactive, then the production of chlorides is simply a manifestation of the indiscriminate nature of the more energetic cations. Accordingly, abstraction of chloride from the solvent by the cubyl and 1-bicyclo[2.2.1]heptyl cations is seen to be competitive with their capture by fluoride ion. Furthermore, the different ratios observed in the case of the cubyl and 1-bicyclo[2.2.1]heptyl systems is a reflection of the relative stabilities of the corresponding cations, a measure of which is provided by the knowledge that cubyl triflate (**14**) solvolyzes much more readily than 1-bicyclo[2.2.1]heptyl triflate (**13**). It is highly significant that the solvolytic behavior of **13** and **14** is reinforced by the results of *ab initio* calculations at the MP2/6-31G*//RHF/3-21G level. In the latter context, Hrovat and Borden[6] have determined that the cubyl cation requires considerably less energy for its formation than does the 1-norbornyl cation.


1, X = I
4, X = F


2, X = I
5, X = F

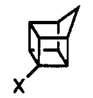

3, X = I
6, X = F

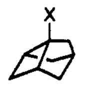

7, X = I
9, X = F
11, X = Cl
13, X = OTf


8, X = I
10, X = F
12, X = Cl
14, X = OTf


15, X = I
19, X = F
29, X = Cl
33, X = OTf


16, X = I
20, X = F
30, X = Cl
34, X = OTf


17, X = I
21, X = F
31, X = Cl
35, X = OTf


18 X = I
22, X = F
32, X = Cl
36, X = OTf

In the interim we have been attempting to extend the fluorodeiodination procedure to the synthesis of other caged bridgehead fluorides, viz., 6-fluorotricyclo[3.1.1.0^{3,6}]heptane (**19**), 1- and 4-fluorohomocubane (**20**) and (**21**),

---

• Abstract published in *Advance ACS Abstracts*, November 15, 1993.

[1] Flinders University.

[2] University of Melbourne.

[3] Della, E. W.; Head, N. J. *J. Org. Chem.* **1992**, *57*, 2850.

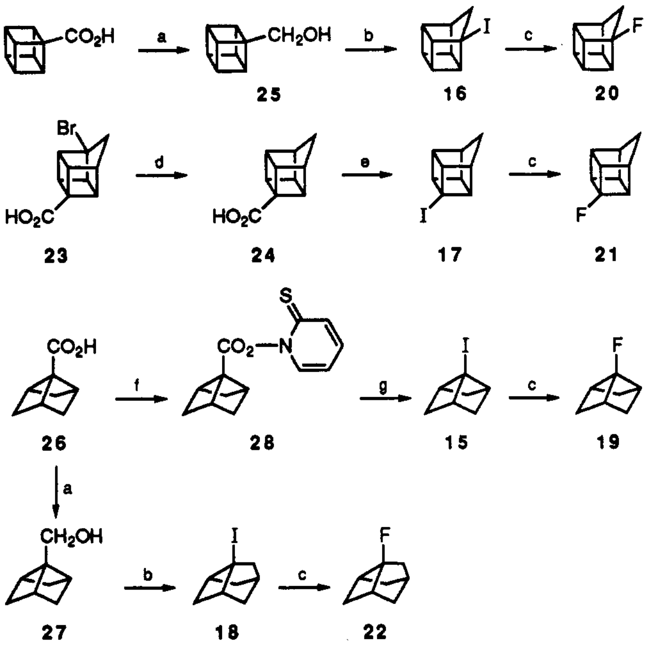
[4] (a) Eaton, P. E.; Yang, C.-X.; Xiong, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3225. (b) Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1990**, *112*, 3228.

[5] Sherrod, S. A.; Bergman, R. G.; Gleicher, G. J.; Morris, D. G. *J. Am. Chem. Soc.* **1972**, *74*, 4615.

[6] Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 3227.

0022-3263/93/1958-7876$04.00/0

Scheme II[a]



[a](a) $LiAlH_4$; (b) (1) Ph_3PI_2, (2) silica gel; (c) XeF_2; (d) Bu_3SnH, AIBN, hν; (e) $Pb(OAc)_4$, I_2, hν; (f) $HONC_5H_4S$, DCC; (g) CF_3CH_2I, CH_2Cl_2, hν.

and 6-fluorotricyclo[3.2.1.0^{3,6}]octane (**22**) from their iodides **15**–**18**. We now wish to report the results of this investigation, and, in view of several interesting observations made during the course of these experiments, we also present details of some *ab initio* calculations we have undertaken on the corresponding caged cations.

Results and Discussion

The precursor iodides new to this study were obtained via the reactions depicted in Scheme II. The acid **24** was converted into the corresponding iodide **17** in high yield (90%) with lead tetraacetate and iodine.[3] However, owing to its volatile nature, iodide **15** was synthesized more conveniently via Barton ester methodology.[3] 1-Iodohomocubane (**16**) and 6-iodotricyclo[3.2.1.0^{3,6}]octane (**18**) were prepared by taking advantage of the propensity of the hydroxymethyl derivatives **25** and **27** to undergo Wagner–Meerwein rearrangement. Thus, the carbinols **25** and **27** were readily transformed into the ring-expanded iodides **16** and **18**, respectively, with triphenylphosphine diiodide and silica gel.

Conversion of the iodides **7** and **8** into their corresponding fluorides has been described previously,[3] and, under the relatively mild conditions employed, 4-iodohomocubane (**17**) was found to give the fluoride **21** rapidly in high yield without contamination. The reactive nature of **17** toward fluorination is not surprising in view of the comparable rates of solvolysis of 4-homocubyl triflate (**35**)[7] and cubyl triflate (**14**).[4] The triflate **35** actually solvolyzes 1 order of magnitude faster that **14** suggesting that production of the corresponding carbocation **41** from iodide **17** should be even more facile than that of the cubyl cation **38** from **14**. The related iodides **15**, **16**, and **18**, however, proved to be highly resistant to fluorination under these conditions. It was found that only under more drastic conditions, viz., by exposure to xenon difluoride at rather higher temperatures and for extended periods of time, could these iodides be induced to react. Even then, 6-iodotricyclo[3.2.1.0^{3,6}]octane (**18**) proved to be practically inert. The product in these cases was shown to consist of mixtures of the desired fluoride and the corresponding chloride. Identification of the components was performed by GC-MS and, for the chlorides, by comparison with authentic samples.

Table I. Products of Fluorodeiodination of the Caged Iodides 7, 8, 15–18

substrate	products (RF/RCl)[a]	normalized solvolysis rates[b]
7	9, 11 (75:25)	1.4×10^{-4}
8	10, 12 (94:6)	1.5×10^{-1}
15	19, 29 (72:28)	na[c]
16	20, 30 (62:38)	na[c]
17	21, 31 (95:5)	1
18	22, 32 (60:40)	na[c]

[a] Given as percentage ratios to facilitate comparisons. These are not yields. [b] For details see Müller, P.; Milin, D. *Helv. Chem. Acta* 1991, *74*, 1808. [c] Not available.

Clearly, the viability of fluorodeiodination as a synthetic procedure to the systems under study here has validity only in the case of iodides **7**, **8**, and **17**. For the other iodides, the major product was a dark intractable oil, and the fluoride/chloride mixture was isolated as a minor product.

As the data in Table I illustrate, the proportion of the chlorides **29**, **30**, and **32** accompanying the fluorides **19**, **20**, and **22** can be quite significant, particularly in the case of the 1-homocubyl and 6-tricyclo[3.2.1.0^{3,6}]octyl systems. Interestingly, the ratio of halides **21** and **31** produced in the reaction of 4-iodohomocubane with xenon difluoride is comparable with that obtained from iodocubane. This observation is predictable in light of the similar rates of solvolysis of 4-homocubyl triflate (**35**)[7] and cubyl triflate (**14**)[4] as discussed above.

Unfortunately, it was not possible to test the existence of a correlation between the fluoride/chloride ratios from fluorodeiodination of the iodides **15**, **16**, and **18** and the rates of solvolysis of the triflates **33**, **34**, and **36** because the latter information is unavailable. While we acknowledge the danger of drawing conclusions from the composition of a minor identifiable product of a reaction and that the ratio of chloride to fluoride in these reactions must therefore be regarded as tenuous, nevertheless the high proportion of chloride obtained in these cases, leads us to suggest that the corresponding cations must be of high energy. Support for this premise is provided by the associated observation that the precursor bridgehead iodides in question are so much less reactive toward the reagent. Accordingly, we predict that the triflates **33**, **34**, and **36** will be most reluctant to undergo the S_N1 process.

In the absence of solvolytic data for these systems, and as an alternative guide to the relative energies of the cations **37**–**42**, we sought recourse to the Hrovat–Borden approach[6] for the determination of MP2/6-31G*//RHF/3-21G energies of the cations in an attempt to provide a theoretical basis for the observed fluorodeiodination product compositions.


37


38


39


40


41


42

Geometries of the cations (**39**–**42**) and corresponding hydrocarbons were optimized at the RHF/3-21G *ab initio*

---

(7) Mergelsberg, I.; Langhals, H.; Rüchardt, C. *Chem. Ber.* 1983, *116*, 360.

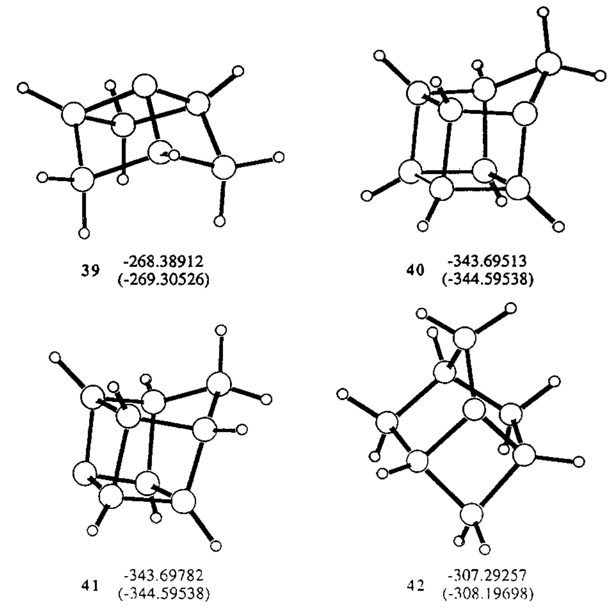


Figure 1. Depicting the RHF/3-21G geometries and energies of the caged cyclobutyl cations **39–42** in this study. Energies of the corresponding hydrocarbons are in parentheses (energies are in hartrees: 1 hartree = 627.5 kcal mol^{-1}).

Table II. Calculated Energies[a] (RHF/6-31G*//RHF/3-21G and MP2/6-31G*//RHF/3-21G) of the Cations (39–42) and Corresponding Hydrocarbons in This Study

structure	*E*(RHF)[b] (R$^+$)	*E*(MP2)[c] (R$^+$)	*E*(RHF)[b] (RH)	*E*(MP2)[c] (RH)
39	-269.90205	-270.78651	-270.80276	-271.70799
40	-345.61187	-346.74340	-346.50211	-347.66230
41	-345.61893	-346.76577	-346.50211	-347.66230
42	-309.00851	-310.01952	-309.90173	-310.94392

[a] Energies in hartress (1 hartree = 627.5 kcal mol^{-1}). [b] RHF/6-31G*//RHF/3-21G energy. [c] MP2/6-31G*//RHF/3-21G energy.

level of theory using standard gradient minimization techniques[8] within the Gaussian 92 system of programs.[9] Structures were identified as energy minima on the appropriate potential energy surface by the evaluation of the complete set of harmonic force constants in each case. In addition, as polarization functions[8] and electron correlation are important for an accurate description of strained, nonclassical ions,[6,8] single point RHF/6-31G*//RHF/3-21G and MP2/6-31G*//RHF/3-21G calculations were performed on the 3-21G-optimized structures. Data for the bicyclo[2.2.1]hept-1-yl (**37**) and cubyl (**38**) cations were taken from the work of Hrovat and Borden.[6]

RHF/3-21G-optimized structures of cations (**39–42**) are displayed in Figure 1, while the calculated energies of the cations (R$^+$) and the corresponding hydrocarbons (RH) at the various levels of theory are listed in Table II.

By employing the procedure reported by Hrovat and Borden,[6] the RHF/6-31G*//RHF/3-21G- and MP2/6-31G*//RHF/3-21G-calculated differences in energy between the cation and parent hydrocarbon relative to the same difference in the *tert*-butyl system[10] (E(RHF), E(MP2)) are listed in Table III along with the percentage bridgehead chloride produced in the corresponding fluorodeiodination reactions (Table I).

Table III. RHF/6-31G*//RHF/3-21G and MP2/6-31G*//RHF/3-21G Energies[a] for the Formation of Cations 37–42 (RH → R$^+$) Relative to the Energy Required for the Formation of *tert*-Butyl Cation and Percentage Bridgehead Chloride Produced in the Fluorodeiodination Reactions

cation	*E*(RHF)	*E*(MP2)	% Cl[b]
37	15.6	14.9	25
38	20.2	7.6	6
39	27.9	20.8	28
40	21.3	19.2	38
41	16.9	5.2	4
42	23.2	22.7	40

[a] Energies in kcal mol^{-1}. [b] In the fluoride/chloride mixture.

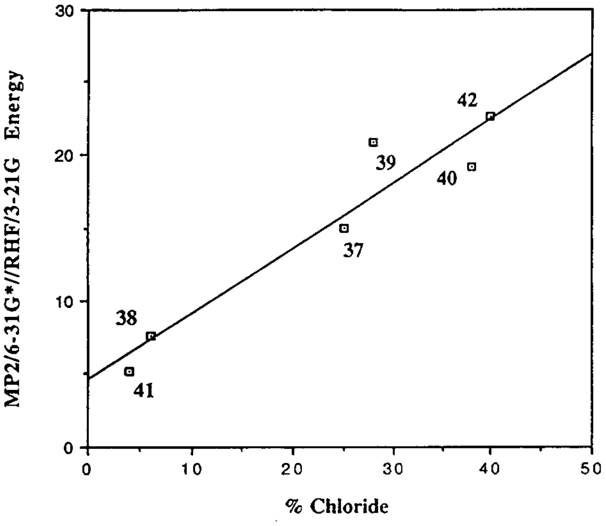


Figure 2. MP2/6-31G*//RHF/3-21G Energies of the cations **37–42** as a function of percentage chloride produced in fluorodeiodination of the corresponding iodides.

Inspection of Table III reveals a large range in the calculated energies for the formation of the caged ions (**37–42**), especially when electron correlation is included and that the cubyl and 4-homocubyl cations (**38**, **41**) are most affected by the inclusion of electron correlation; E(MP2) in the former is found to be 12.6 kcal mol^{-1} less than E(RHF), while the similar difference for the latter is calculated to be 11.7 kcal mol^{-1}. These data support the notion that both **38** and **41** have substantial nonclassical structures.[6,8] The norcubyl ion (**39**) is affected by the inclusion of electron correlation to a lesser degree, with E(MP2) being 7.1 kcal mol^{-1} less than E(RHF). The small changes in energies of the remaining structures **40** and **42** are indicative of substantially less nonclassical character and, consequently, less stabilization in these cations.

A strong correlation is observed (Figure 2) when the percentage chloride produced in the fluorodeiodination reactions (Table I) is plotted against the MP2/6-31G*//RHF/3-21G-calculated energies for the formation of the ions **37–42** (E(MP2)). The correlation found in Figure 2 suggests that not only have the calculations presented in this work provided an accurate ordering of the relative energies the caged cations (**37-42**), but in addition it supports the suggestion that the cations of high energy

---

[8] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, P. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[9] 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.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92, 1992, Revision F, Gaussian Inc., Pittsburgh, PA. Calculations were performed on a SUN SparcStation 2 computer, except for MP2/6-31G** which were performed on a Cray Y-MP4E/364 computer.

[10] Calculated energies of the *tert*-butyl cation are −156.44234 and −156.93950 Hartrees at the RHF/6-31G*//RHF/3-21G and MP2/6-31G*//RHF/3-21G levels of theory, respectively, while the corresponding energies for 2,2-dimethylpropane are −157.29866 and −157.82781 Hartrees, respectively.

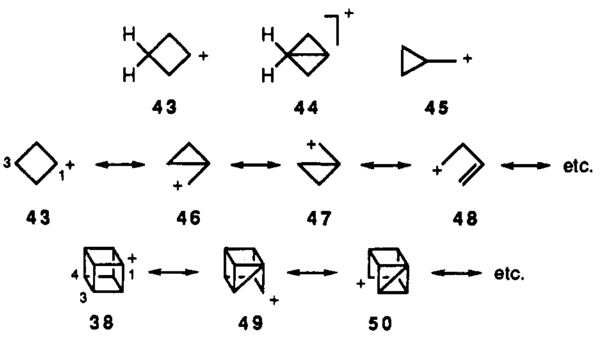
are also less discriminating in their behavior toward nucleophilic reagents.

What is the rationale for the large range of MP2-derived energies for the caged ions **38**–**42**? Furthermore, how do we account for the observation that the calculated energies do not follow the trend anticipated on intuitive grounds? For example, while the cubyl cation must accommodate the most highly distorted geometry at the positively-charged site it, along with **41**, is seen to possess the greatest degree of stabilization.

Inspection of the group of polycyclic cations (**38**–**42**) reveals that a common feature of all the systems is the presence of a cyclobutyl cation moiety. The cyclobutyl cation (**43**) is endowed with enhanced thermodynamic stability (see below) and the logical inference is that the caged structures (**38**–**42**) should, as a consequence, possess considerable stabilization. Clearly this is not the case; as noted above both the cubyl and 4-homocubyl cations are much more stable than the other ions.

The cyclobutyl cation has recently attracted considerable attention from theoretical chemists. High level *ab initio* calculations suggest that **43** is more accurately described by the bicyclobutonium structure **44**, in which favorable cross-ring (*through-space*) interactions are of major importance.[11-14] These calculations also predict that **44** is in rapid equilibrium with the cyclopropylcarbinyl isomer **45** over a rather flat energy surface in which both structures have similar energy. Such stabilization available to the cyclobutyl ion can be represented by resonance structures (**46**–**48**). In molecular orbital terms, these cannonical structures represent the symmetric combination of the C2–C3 (α,β) and C3–C4 (β,α) bonds in **43** which are hyperconjugatively delocalized toward the cationic center. This view is supported by the MP2/6-31G* *ab initio* calculations which predict a short C1–C2 bond (1.424 Å), a long C2–C3 bond (1.649 Å), and substantial C1–C3 bonding (1.650Å).[11] Interestingly, Koch found that the minimum level of theory capable of accurately describing the bicyclobutyl cation **44** was MP2/6-31G*.[12]

Similar bonding, but now also including β,γ (C–C) hyperconjugation, has recently been ascribed by Eaton[4a,15] to be involved in the cubyl cation, which can be represented by the resonance structures (**49**–**50**). Eaton's suggestion has strong support from the *ab initio* calculations of Hrovat and Borden.[6] Rüchardt and co-workers have postulated similar factors to be responsible for the stability of the 4-homocubyl cation **41**.[7]



We speculate that a balance of unfavorable strain on the one hand and favorable nonclassical hyperconjugative stabilization on the other to be responsible for the overall stability of each of the caged cyclobutyl cations in this study. The cations fall into two categories: those in which the formal cationic center is at the bridgehead of three cyclobutyl rings (**38**, **39**, and **41**), and those in which the cationic center is at the junction of three rings of which only one is four-membered (**40** and **42**).

Inasmuch as the 1-homocubyl and 6-tricyclo[3.2.1.$0^{3,6}$]-octyl cations (**40** and **42**) are stabilized by the interaction of just one four-membered ring , the overall stability of these ions may reasonably be expected to be influenced strongly by unfavorable strain. Our calculational and experimental data are in agreement with this expectation and indicate that these two systems are of high energy.

On the other hand, **38**, **39**, and **41** possess similar geometries at the formal cationic center and, given that these cations are stabilized by the nonclassical interaction of three cyclobutane rings, one might expect all three to possess considerable stability. Only the cubyl and 4-homocubyl cations (**38**, **41**), however, are found to be substantially stabilized.

This apparent anomaly prompted further investigation by high-level *ab initio* techniques. Consequently, the geometries of the cubyl and norcubyl ions (**38**, **39**) were fully optimized at the MP2/6-31G** level of theory along with those of the parent hydrocarbons cubane (**51**) and norcubane (**52**). The optimized geometries of these species are displayed in Figure 3 along with the charge distribution (cations) and overlap populations derived from Mulliken population analysis of the MP2/6-31G**-calculated wavefunction in each case.

Inspection of Figure 3 reveals some interesting features. Firstly, these calculations predict that the charge in the cubyl cation **38** is substantially delocalized away from the formal cationic center (+0.12) to the α- and γ-positions (+0.20, +0.15) with little charge buildup at the β-position (+0.04). In addition, the C1–C(α) bond populations are found to be identical in both **38** and the corresponding hydrocarbon **51**. The α,β bonds are found to be slightly longer while the β,γ bonds show little change in length in the cation compared with those in the parent hydrocarbon (cubane). In addition, the α,β and β,γ bonds are found to be noticeably less populated in the cation, with bond populations of 0.21 and 0.24, respectively, over that found in cubane (0.29). Significantly, the cross-ring C1–C(β) interaction in the cation, with a population of –0.01, is predicted to be essentially nonbonding and substantially less antibonding than in the hydrocarbon; the similar interaction in **51** is calculated to have a population of –0.10.

The charge in the norcubyl ion (**39**), on the other hand, is found to be delocalized in a different manner to that found in **38**. Our calculations predict that the charge in **39** is delocalized to the β-position (+0.18), with little charge buildup at the α-position (+0.07); the formal cationic center maintains a charge of +0.23. In addition, population analysis reveals substantial shortening of the C1–C(α) bonds (1.484 Å) in the cation over the hydrocarbon **52** (1.569 Å) with a corresponding increase in overlap population (0.29 *vs* 0.24). These same calculations also reveal a lengthening of the α–β bonds in the cation (1.567 Å *vs* 1.541 Å) with a corresponding decrease in overlap population (0.25 *vs* 0.29). Interestingly, unlike the cubyl

---

[11] McKee, M. L. *J. Phys. Chem.* **1986**, *90*, 4908.

[12] Koch, W.; Liu, B.; DeFrees, D. J., *J. Am. Chem. Soc.* **1988**, *110*, 7325.

[13] Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652.

[14] Saunders, M.; Jiminez-Vazquez, H. A. *Chem. Rev.* **1991**, *91*, 375.

[15] (a) Eaton, P. E. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1421. (b) Eaton, P.E.; Zhou, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 3118.

[16] Cole, T. W., Jr. Ph.D. Disertation, University of Chicago, Chicago, IL, 1966.

system, **39** is calculated to contain substantially less cross-ring stabilization; the C1–C(β) overlap population in **39** is calculated to be –0.10, significantly more antibonding than the corresponding interaction in **38** and only marginally less that the similar interaction in norcubane (**52**) (–0.13).

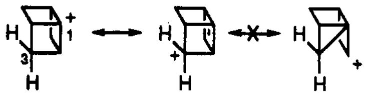
The MP2/6-31G** calculations for both **38** and **39** show little participation of the carbon–hydrogen bonds in the overall stabilization process as evidenced by the lack of appreciable change in C–H populations in the cation over the parent hydrocarbon in each case; this is as expected given that these bonds are substantially stronger and of significantly lower energy than the strained carbon–carbon bonds in the four-membered rings in each system.

In resonance terms, these calculations support the view that the cubyl cation (**38**) is best represented by the canonical structures (**38**, **49–50**), as suggested by Eaton,[4a] with **53** being of little importance. In contrast, the norcubyl ion (**39**) appears best represented by cannonical structures (**39**, **54**), with structure **55** being of little importance.

51

52

53



39 **54** **55**

Why should these apparently similar ions be stabilized by significantly different mechanisms? The answer to this question, we believe, lies in the nature of the four-membered charge-bearing rings in each case.

At position 3(β) in the cubyl cation there are three carbon–carbon bonds. Resonance structures **49** and **50** represent a linear combination of the α,β and β,γ C–C bonding orbitals which are delocalized toward the cationic p-orbital in **38**. If these orbitals contribute approximately equally to this combination, as depicted in Figure 4, then the resultant orbital (ψ) subtends an angle (θ) of approximately 110° with the vacant p-orbital, sufficient for the overlap required in the nonclassical representation of **38**. The α,β C–C bonds in **38**, on the other hand, subtend a twist angle (ω) of about 45° with the vacant p-orbital and is not conducive to the formation of the π-bond required in canonical structure **53**.

In contrast, the norcubyl system **39** is deficient in strained β,γ C–C bonds and must rely on the linear combination of the two α,β bonds at position 3 (β) in order to achieve the bonding required in resonance structure **55**. Inspection of the calculated geometry of **39** clearly indicates that the resultant orbital (ψ) obtained in this manner is not directed toward the vacant cationic p-orbital at position 1 (Figure 4). Unlike the cyclobutyl cation (**43**), the rigid geometry of the norcubyl system prevents this cation from adopting a conformation more conducive to this overlap; as a consequence, canonical structure **55** cannot play an important role in the overall stability of **39**. In addition, the α,β bonds in **39** subtend a twist angle (ω) of about 56° with the vacant p-orbital, even less conducive to the formation of the π-bond required in **54** than was observed for the cubyl cation (**38**), and consequently involving considerable strain.

The existence of the γ-carbon therefore appears to be significant in the stabilization mechanism available to the cubyl (and presumably 4-homocubyl) cation; the norcubyl ion, lacking appropriate strained β,γ C–C bonds is, as a result, significantly less stable than either **38** or **41**.

Conclusions

Ab initio calculations with the inclusion of electron correlation (MP2/6-31G*//RHF/3-21G) provide evidence that strain and the nature of the four-membered charge-bearing rings present are the major factors contributing to stabilization in the caged bridgehead cyclobutyl cations in this study. The cubyl and 4-homocubyl cations (**38**, **41**), each containing three cyclobutyl cation fragments, are found to be extensively stabilized. The norcubyl ion (**39**), which also contains three cyclobutyl cation fragments, would appear to be (anomalously) somewhat less stabilized. A comparison between the cubyl and norcubyl ions (**38**, **39**) using high-level MP2/6-31G** calculations (full optimization) reveals that **39** is stabilized in a different manner to **38** and (presumably) **41**, the absence of the interaction of a strained β,γ C–C bond in **39** being primarily responsible for its decreased stability.

The remaining ions (**40**, **42**), which contain a single cyclobutyl cation moiety, are predicted to be substantially less stabilized by these interactions, and their overall thermodynamic stability is determined largely by strain.

On the basis of the above calculations we predict that the triflates of the 6-tricyclo[3.1.1.0^{3,6}]heptyl, 1-homocubyl, and 6-tricyclo[3.2.1.0^{3,6}]octyl systems, viz. **33**, **34**, and **36**, will be found to be most reluctant to undergo solvolysis. Work is currently in progress to provide an experimental test of these predictions.

Experimental Section

All melting points and boiling points are uncorrected. Melting points were determined using a Reichart hot stage apparatus. Routine ^{1}H NMR spectra were obtained on a Hitachi RS-1200 spectrometer. ^{13}C data were collected on a Varian Gemini 300BB instrument operating at 75.46 MHz. NMR measurements were determined in $CDCl_3$ solution unless otherwise stated, and chemical shifts relative to TMS are reported in ppm (δ), along with assignments in parentheses. Abbreviations used: s (singlet), d (doublet), J (coupling constant). Mass spectra and high-resolution mass spectra (HRMS) were recorded on a Kratos M25RF spectrometer operating at an ionizing voltage of 70eV. Selected fragment ions are reported as their mass/charge ratio (m/z) followed by their relative intensities as compared to the base fragment in parentheses. Chromatographic samples were introduced via a Carlo Erba GC 6000 chromatograph equipped with an Altech Associates RSL-150 (0.32 mm × 25 m) fused silica column. Analytical GC was performed on a Perkin-Elmer 8410 chromatograph using an Altech Associates RSL-300 (0.53 mm × 30 m) fused silica column. Elemental analyses were carried out by the Australian Microanalytical Service. The homogeneity of all sublimed/distilled compounds was established by GC analysis. Cubylcarbinol (**25**),[16] 1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylic acid (**23**),[17] tricyclo[3.1.1.0^{3,6}]heptane-6-carboxylic acid (**26**),[18] and tricyclo[3.1.1.0^{3,6}]heptane-6-methanol (**27**)[19] were prepared by the designated literature procedures.

1-Iodopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (16). To a solution of the carbinol **25** (1.0 g, 7.5 mmol) and triphenylphosphine (3.9 g, 15 mmol) in CH_2Cl_2 (8.0mL) at 0 °C was added a solution of iodine (3.75 g, 15 mmol) in CH_2Cl_2 (35 mL). The mixture was stirred at 0 °C for 3 h and then refluxed for 2 h. The reaction mixture was cooled and poured onto pentane (100 mL). The pentane solution was washed with sodium metabisulfite solution

---

[17] Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1972**, *28*, 4131.

[18] Monti, S. A.; Harless, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 2690.

[19] Della, E. W.; Janowski, W. K.; Pigou, P. E. *Aust. J. Chem.* **1992**, *45*, 1205.

[20] Luh, T.-Y.; Stock, L. M. *J. Org. Chem.* **1977**, *42*, 2790.

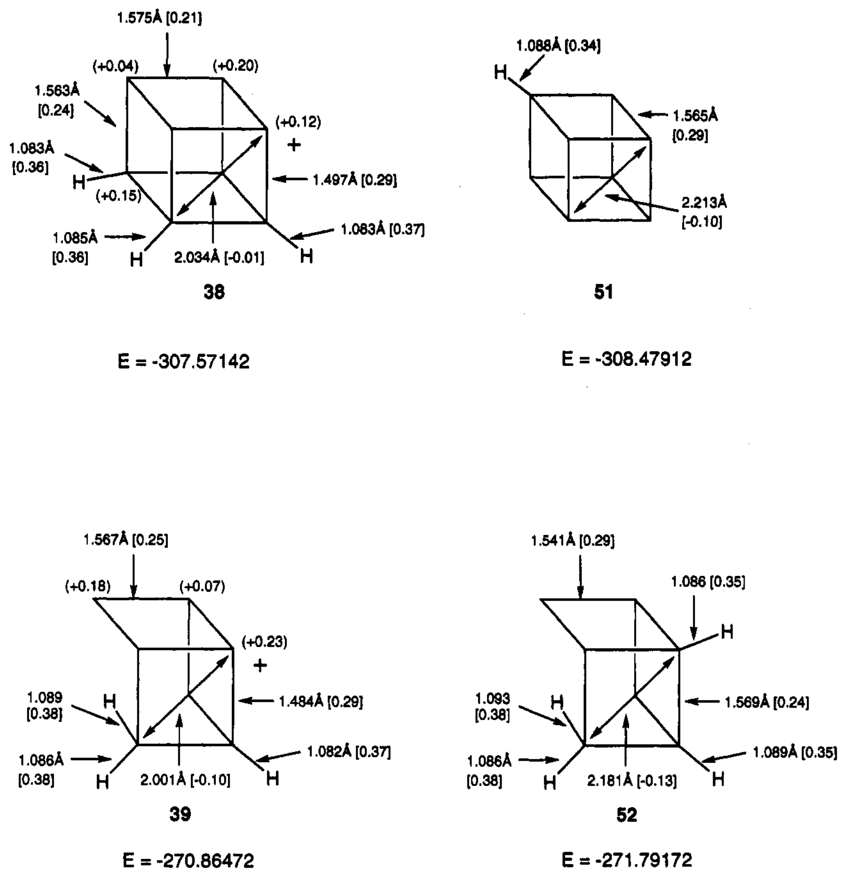


Figure 3. MP2/6-31G**-Optimized geometries, energies, charge distribution (parentheses) and (Mulliken) bond electron populations [square papentheses] in the cubyl and norcubyl cations (**38**, **39**), cubane and norcubane (**51**, **52**) (energies in hartrees: 1 hartree = 627.5 kcal mol^{-1}).

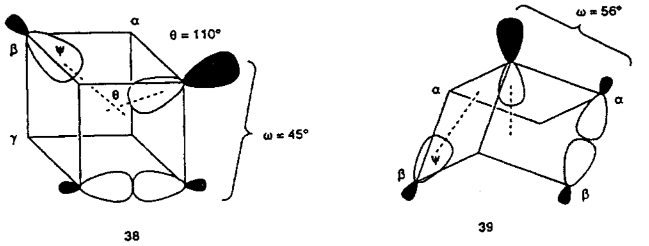


Figure 4. Depicting the hyperconjugative interactions in the cubyl and norcubyl cations (**38** and **39**).

(3 × 50 mL) and water (2 × 50 mL) and then dried ($MgSO_4$) and concentrated to dryness *in vacuo* at room temperature. The residue was triturated with pentane, and the pentane extracts were added to a mixture of silica gel (16 g) and pentane (40 mL) and stirred overnight. The pentane was evaporated at room temperature and the silica gel transferred to a chromatography column. The material which was eluted with pentane was distilled (kugelrohr: 115–120 °C/6 mm) to give **1-iodopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (16)** (1.1g, 61%): ^{1}H NMR ($CDCl_3$) δ 2.18 (d, 2H, *J* = 1.1Hz, CH_2), 2.87–3.60 (m, 7H, cage); ^{13}C NMR ($CDCl_3$) δ 57.18, 55.28, 51.26, 46.28, 43.38, 42.47, 39.04; mass spectrum *m/z* (rel inten) 244 (2), 193 (7), 117 (86), 116 (55), 115 (100), 91 (47); HRMS calcd for C_9H_9I $[M]^{+\cdot}$ 243.9748, found 243.9771. Anal. Calcd for C_9H_9I: C, 44.3; H, 3.7. Found: C, 44.1; H, 3.8.

Pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylic acid (24). A solution of the bromo acid **23** (600 mg, 2.49 mmol) and AIBN (catalytic quantity) in THF (40 mL) was treated with tributyltin hydride (1.2 mL, 3.3 mmol) at 0 °C for 3 h while under irradiation (300-W tungsten lamp).[20] The solvent was evaporated and the residue taken up in ether (40 mL). The ether solution was extracted with 10% aqueous sodium hydroxide (2 × 20 mL) and the basic extracts were then washed with a fresh portion of ether (20 mL). The aqueous phase was acidified (pH 1) with concd HCl, and the precipitate which formed was extracted with ether (3 × 30 mL). The ether was dried ($MgSO_4$) and evaporated. Sublimation (kugelrohr: 100 °C/0.02 mm) of the crude product gave pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylic acid (**24**) (397 mg, 98%), mp 92 °C (lit.[21] 93–95 °C).

4-Iodopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (17). The acid **24** (650 mg, 4.0 mmol) was treated with lead tetraacetate and iodine as previously described for the preparation of iodocubane.[3] After a standard workup, the crude product was distilled (kugelrohr: 115–120 °C/6 mm) and afforded **4-iodopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (17)** as a colorless oil (870 mg, 90%): ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 2H, CH_2), 3.28–3.80 (m, 7H, cage); ^{13}C NMR ($CDCl_3$) δ 55.80, 52.08, 45.49, 45.17, 43.65, 43.51, 33.90. Anal. Calcd for C_9H_9I: C, 44.3; H, 3.7. Found: C, 44.4; H, 3.4.

6-Iodotricyclo[3.1.1.0^{3,6}]heptane (15). The carboxylic acid **26** (690 mg, 5 mmol) was converted to the iodide **15** by the Barton ester route previously described[3] (method B, solvent: CH_2Cl_2). Distillation (kugelrohr: 80 °C/3 mm) of the crude product yielded the iodide **15** (850 mg, 77%) whose ^{1}H NMR data were in accord with those previously reported:[22] ^{13}C NMR ($CDCl_3$) δ 46.75, 37.79, 36.28.

6-Iodotricyclo[3.2.1.0^{3,6}]octane (18). A mixture of tricyclo[3.1.1.0^{3,6}]heptane-6-methanol (**27**) (0.36 g, 3.0 mmol) and triphenylphosphine (0.8 g, 3.3 mmol) in dry DMF (3 mL) was stirred at 25 °C for 30 min, after which it was cooled to −10 °C and treated dropwise over 20 min with a solution of iodine (0.84 g, 3.3 mmol) in DMF (1mL). The reaction mixture was stirred overnight at 25 °C and then added to water. The aqueous mixture was extracted with pentane, and the organic extract washed with aqueous sodium metabisulfite solution before being dried ($MgSO_4$) and evaporated. The oily residue was chromatographed (silica gel); distillation (kugelrohr: 115 °C/7 mm) of the material eluted with pentane yielded **6-iodotricyclo[3.2.1.0^{3,6}]octane (18)**

---

(21) Dunn, G. L., Dipasquo, V. J.; Hoover, J. R. E. *J. Org. Chem.* **1968**, *33*, 1455.

(22) Abeywickrema, R. S.; Della, E. W. *J. Org. Chem.* **1980**, *45*, 4226.

(0.15 g, 22%): ^{1}H NMR (CDCl$_3$) δ 1.07–2.90 (m, 11H); ^{13}C NMR (CDCl$_3$) δ 52.41, 45.57, 40.55, 39.04, 38.19, 35.16; mass spectrum *m/z* (rel inten) 234 (27), 206 (23), 192 (39), 189 (23), 163 (26), 149 (24), 142 (30), 128 (33), 107 (61), 95 (39), 91 (83), 85 (31), 77 (84), 71 (42), 66 (100); HRMS calcd for $C_8H_{11}I$ $[M]^{+\cdot}$ 233.9905, found 233.9901. Further elution with ether yielded starting material **27** (0.15 g, 42%).

Reaction of 1-Iodopentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (16) with XeF$_2$. A vessel containing a solution of the iodide **16** (73 mg, 0.3 mmol) and XeF$_2$ (76 mg, 0.45 mmol) in CH$_2$Cl$_2$ (2 mL) was sealed and heated in an oil bath at 70 °C overnight. After workup,[3] GC-MS analysis showed the volatile portion of the reaction mixture to consist of a 62:38 mixture of **1-fluoropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}0^{4,7}$]nonane (20)**: ^{13}C NMR (CDCl$_3$) δ 45.8 (d, J(CF) = 17.4Hz), 45.1 (d, J(CF) = 19.1Hz), 44.0 (d, J(CF) = 7.4Hz), 42.2 (d, J(CF) = 2.4Hz), 41.0, 38.8 (d, J(CF) = 11.8Hz); mass spectrum *m/z* (relative intensity) 135 $[M\text{-}1]^{+\cdot}$ (100), 133 (18), 116 (17), 115 (45), 109 (41), 96 (8), 91 (7), 83 (12), 57 (9), 53 (12), 52 (14), and 1-chloropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (**30**) whose identity was established by comparison with authentic material **30** prepared below.

4-Fluoropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (21). The iodide **17** (816 mg, 3.34 mmol) in CH$_2$Cl$_2$ (22 mL) was treated with XeF$_2$ (846 mg, 5.0 mmol) at room temperature as previously described[3] for the synthesis of fluorocubane. The reaction mixture was stirred for 3 h after which time the the iodide **17** had been completely consumed (GC). Following a standard workup, the solvent was removed by distillation through a packed column. Distillation of the residue and collection of the distillate in a cold trap (−100 °C) afforded **4-fluoropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (21)** (407 mg, 89%): ^{1}H NMR (CDCl$_3$) δ 1.71 (d, J = 1.14 Hz, 2H, CH$_2$), 2.89–3.88 (m, 7H, cage); ^{13}C NMR (CDCl$_3$) δ 97.36 (d, J(CF) = 322.0 Hz), 41.49 (d, J(CF) = 12.13 Hz), 40.52 (d, J(CF) = 4.93 Hz), 53.04 (d, J(CF) = 23.91 Hz), 50.57 (d, J(CF) = 24.99 Hz); mass spectrum *m/z* (rel inten) 136 (17), 135 (100), 133 (19), 116 (10), 115 (26), 110 (15), 109 (57), 97 (20), 96 (14), 91 (13); HRMS calcd for C_9H_8F $[M-1]^{+\cdot}$ 135.0610, found 135.0629.

Reaction of 6-Iodotricyclo[3.1.1.$0^{3,6}$]heptane (15) with XeF$_2$. A solution of the iodide **15** (367 mg, 1.6 mmol) in dichloromethane (10 mL) was heated with XeF$_2$ as described for the treatment of **16**. The volatile fraction of the product was removed and analyzed by GC-MS which showed the presence of two components in the ratio 72:28; that with the longer retention time was identified as 6-chlorotricyclo[3.1.1.$0^{3,6}$]heptane (**29**) by comparison with authentic material prepared below. The peak with shorter retention time represents the major product and was attributed to **6-fluorotricyclo[3.1.1$0^{3,6}$]heptane (19)**: mass spectrum *m/z* (rel inten) 113 $[M+1]^{+\cdot}$ (19), 102 (6), 100 (17), 93 (72), 91 (100), 87 (25), 77 (93), 65 (24), 51 (22), 39 (18).

Reaction of 6-Iodotricyclo[3.2.1.$0^{3,6}$]octane (18) with XeF$_2$. A solution of the iodide **18** (54 mg, 0.23 mmol) in CH$_2$Cl$_2$ (1.54 mL) was treated with XeF$_2$ as described above for the iodide **15**. Analysis of the volatile portion of the product by GC-MS showed the presence of two components in a 60:40 ratio. The minor constituent had the longer retention time and was identified as 6-chlorotricyclo[3.2.1.$0^{3,6}$]octane (**32**) by comparison with a specimen of **32** prepared below. The peak due to the more volatile constituent (the major product) was attributed to **6-fluorotricyclo[3.2.1.$0^{3,6}$]octane (22)**: mass spectrum *m/z* (rel inten) 127 $[M+1]^{+\cdot}$ (1), 115 (5), 113 (14), 107 (6), 102 (33), 101 (10), 100 (100), 88 (2), 79 (13), 77 (11), 65 (18), 51 (4), 39 (7).

6-Chlorotricyclo[3.1.1.$0^{3,6}$]heptane (29). Tricyclo[3.1.1.$0^{3,6}$]heptane-6-carboxylic acid (**26**) (0.40 g, 3.0 mmol) was treated according to the conditions described above for the conversion of the acid **24** into its chloride **31**. Workup followed by distillation (kugelrohr: 90 °C/20 mm) of the residue afforded **6-chlorotricyclo[3.1.1$0^{3,6}$]heptane (29)** (0.13 g, 21%): ^{1}H NMR (CFCl$_3$) δ 2.12–2.32 (m, 3H), 2.90–3.07 (m,6H); ^{13}C NMR (CDCl$_3$) δ 72.89, 44.49, 34.70; mass spectrum *m/z* (rel inten) 128 (5), 115 (13), 113 (23), 93 (100), 91 (79), 87 (37), 79 (34), 77 (89), 65 (38); HRMS Calcd for $C_7H_7{}^{35}Cl$ $[M]^{+\cdot}$ 128.0393, found 128.0397.

1-Chloropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (30). To a solution of the iodide (**16**) (1.0 g, 4.1 mmol) in pentane/ether (3:2, 50 mL) was added dropwise at −78 °C a 1.7 M solution of *tert*-butyllithium in pentane (9.6 mL, 16.3 mmol). The mixture was held at −70 °C for 10min and then carbon dioxide was bubbled through the solution as it was allowed to warm to room temperature. The mixture was extracted with 10% aqueous NaOH (3 × 40 mL) and the basic extracts were backwashed with ether (2 × 30 mL). The basic solution was acidified with concd HCl, and the precipitate was extracted with ether (3 × 50 mL). Desiccation (MgSO$_4$) and evaporation of the solvent followed by fractional sublimation of the residue (kugelrohr: 90 °C/1 mm) afforded pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-1-carboxylic acid (434 mg, 65%): mp 112–117 °C; ^{1}H NMR δ 2.07 (s, 2H, CH$_2$), 2.96-3.80 (m, 7H, cage), 11.64 (br, 1H, CO$_2$H); ^{13}C NMR δ 41.36, 41.41, 44.95, 45.37, 47.30, 47.36, 59.64; mass spectrum *m/z* (rel inten) 162 (3), 117 (100), 116 (33), 115 (45), 91 (23), 68 (10); HRMS calcd for $C_{10}H_{10}O_2$ $[M]^{+\cdot}$ 162.0681, found 162.0665. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.0; H, 6.2. Found: C, 73.8; H, 6.6. Pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-1-carboxylic acid (65 mg, 0.04 mmol) was subjected to the chlorodecarboxylation procedure described above. Workup followed by column chromatography (silica gel, CHCl$_3$) gave **1-chloropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (30)**: ^{1}H NMR (CDCl$_3$) δ 2.05 (s, 2H), 3.15–3.50 (m, 7H); ^{13}C NMR (CDCl$_3$) δ 72.68, 51.85, 51.29, 45.45, 42.02, 41.56, 40.15; mass spectrum *m/z* (rel inten) 151 (6), 118 (21), 117 (100), 116 (39), 115 (72), 103 (6), 91 (44), 69 (68), 65 (16); HRMS calcd for $C_9H_8{}^{35}Cl$ $[M-1]^{+\cdot}$ 151.0314, found 151.0291.

4-Chloropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (31). A mixture of pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-4-carboxylic acid (**24**) (0.49 g, 3.0 mmol), *N*-hydroxypyridine-2(1*H*)-thione (0.42 g, 3.3 mmol) and dicyclohexylcarbodiimide (0.68 g, 3.3 mmol) in dichloromethane (20 mL) was stirred at 25 °C under a nitrogen atmosphere for 4 h. The precipitated dicyclohexylurea was filtered off and washed with CH$_2$Cl$_2$ (2 × 5mL), and the combined CH$_2$Cl$_2$ solutions were evaporated. The residue was added to CFCl$_3$ (15 mL) and irradiated with a 300-W tungsten lamp under a N$_2$ atmosphere for 4 h. The reaction mixture was cooled to 0 °C and then washed successively with 6 M HCl (2 mL) and water (3 mL). After removal of the solvent, the residue was distilled (kugelrohr: 100 °C/20 mm) to give **4-chloropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (31)** (0.28 g, 46%): ^{1}H NMR (CDCl$_3$) δ 1.7 (s, 2H, CH$_2$), 3.2–3.6 (m, 7H, cage); ^{13}C NMR (CDCl$_3$) δ 66.94, 53.78, 50.60, 45.60, 42.53, 41.85, 41.29; mass spectrum *m/z* (rel inten) 122 (16), 118 (20), 117 (100), 116 (21), 115 (40), 105 (26), 98 (18), 91 (35), 83 (19), 77 (14), 65 (16); HRMS calcd for C_9H_9 $[M-Cl]^{+\cdot}$ 117.0705, found 117.0701.

6-Chlorotricyclo[3.2.1.$0^{3,6}$]octane (32). Tricyclo[3.1.1.$0^{3,6}$]heptane-6-methanol (**27**) (0.15 g, 1.25 mmol) was added to thionyl chloride (1 mL) at 0 °C and the mixture allowed to warm to room temperature and then heated to 70 °C for 15 min. The mixture was cooled and poured carefully onto ice, before being extracted with pentane. The organic layer was washed with sodium bicarbonate solution, dried (MgSO$_4$), and then filtered through a column of silica gel. Evaporation of the solvent and distillation (kugelrohr: 80 °C/40 mm) of the residue yielded **6-chlorotricyclo[3.2.1.$0^{3,6}$]octane (32)** (0.04 g): ^{1}H NMR (CDCl$_3$) δ 1.45–2.50 (m); ^{13}C NMR δ (CDCl$_3$) 75.22, 47.97, 42.13, 39.52, 37.61, 35.15; HRMS Calcd for $C_8H_{11}{}^{35}Cl$ $[M]^{+\cdot}$ 142.0549, found 142.0572.

Acknowledgment. The award of a Flinders University Research Scholarship (to N.J.H.) is acknowledged. We thank the Australian Research Council for financial support.

Supplementary Material Available: Cartesian coordinates of the RHF/3-21G optimized structures of cations **39–42** and MP2/6-31G** optimized structures of **38**, **39**, **51**, and **52**. Copies of ^{13}C NMR spectra of **18**, **21**, and **29–32** and the mixture (**20** + **30**) from the reaction of **16** with XeF$_2$ (16 pages). This material, which is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal and can be ordered from the ACS; see any current masthead for ordering information.