

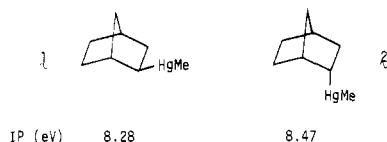
Stereoelectronic Effects on the Protonation and Properties of 2-Norbornyl Chlorides¹

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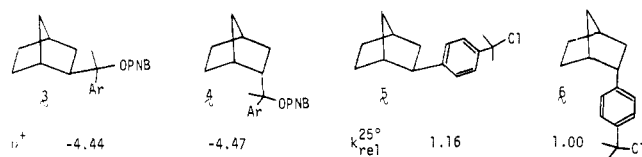
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Abstract: Novel stereoelectronic effects are found to be responsible for differences in many properties computed by the MINDO/3 method for *exo*- and *endo*-2-norbornyl chlorides, **9**–**12**. The lower C–Cl stretching force constant, lower ionization potentials, and higher proton affinities for the *exo* isomers are especially intriguing. The highest occupied molecular orbitals (HOMOs) for the chlorides are found to be perturbed forms of the HOMOs of norbornane or boat cyclohexane which Hoffmann et al. termed the AA ribbon orbital. Increased C–Cl bonding character in the HOMOs of the *exo* isomers cause the lower ionization potentials and may also account for the variation in the force constants. The higher proton affinities for the *exo* chlorides can be attributed to steric hindrance in the protonated *endo* species. Using the protonated chlorides as model ion pairs argues against the viability of a symmetric tight ion pair as an intermediate in the acetolyses of *exo* substrates. The analyses are aided by perturbation theory arguments, extensive comparisons with results for cyclopentyl analogues, and the use of three-dimensional drawings of molecular orbitals.

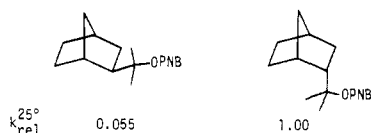
The chemical and physical characteristics of molecules containing the bicyclo[2.2.1]hept-2-yl framework continue to be fascinating topics. Recently, Brown has published a book with extensive comments by Schleyer which summarizes and analyzes in depth the solvolytic behavior of 2-norbornyl derivatives.³ Olah has also reviewed his experimental work on the same systems.⁴ However, the questions in this area involve more than the nature of the 2-norbornyl cation and the origin of the *exo/endo* rate ratio in different media. Stereoelectronic effects responsible for electrophilic attack on the *exo* face of norbornenes have been the subject of substantial current interest.⁵ In addition, Kochi et al. have determined from photoelectron studies that the ionization potential of *exo*-2-norbornylmethyl mercury is significantly lower than for its ep-



imer.⁶ This was interpreted to imply that there is a stereoelectronic preference for an *exo*- over an *endo*-2-norbornyl substituent as an electron donor in the gas phase.⁶ Brown and coworkers have not found compelling evidence for such an effect in solvolyses carried out in 80% acetone.^{3,7} For example, the ρ^+ values for the tertiary, aryl derivatives **3** and **4** are es-

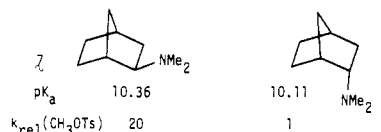


entially identical; and, while the solvolyses rate for the *exo* substituted cumyl chloride (**5**) is trivially faster than for the *endo*, a case can be made for steric acceleration in the solvolysis of the *endo* substituted isopropyl-OPNB.⁷

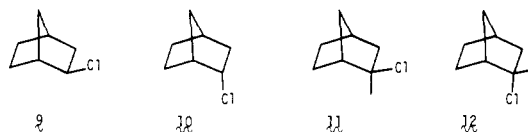


Along similar lines, Menger and Thanos recently found small differences in the pK_a s and rates of quaternization for *exo*- and *endo*-2-dimethylaminonorbornane.⁸ These results are open to interpretation as either a consequence of an electronic effect analogous to Kochi's which would make **7** more

basic, or as a reflection of greater steric restrictions for **8**, or both. Menger and Thanos claim that the data indicate that there is little crowding in the *endo* cavity of **8**.⁸



In the spirit of these latter studies, we have undertaken a search for stereoelectronic and steric effects in the properties of secondary and tertiary 2-norbornyl chlorides (**9**–**12**). The



approach that is followed is a theoretical one featuring MINDO/3⁹ calculations and perturbation theory arguments. In previous work, the reliability of MINDO/3 results for many properties of alkyl chlorides has been found to be good, and certainly comparable with *ab initio* calculations using moderate basis sets.^{2,10,11} In particular, we published two papers contrasting MINDO/3, *ab initio* STO-3G and 44-31G, and experimental data on the properties and geometries of neutral and protonated alkyl chlorides.² Although MINDO/3 is more accurate for dipole moments, force constants, and ionization potentials, the description of protonated alkyl chlorides is better using the STO-3G basis. The computed properties from the extended 44-31G calculations were generally less satisfactory than both STO-3G and MINDO/3 results. Dewar has also recently published an important MINDO/3 study of norbornyl cations that will receive some attention in the following.¹²

A variety of properties have been calculated for **9**–**12** including geometries, relative energies, ionization potentials, dipole moments, C–Cl stretching force constants, and proton affinities. Comparisons with data for cyclopentyl chlorides aid the analyses. The lower C–Cl force constant, lower ionization potentials, and higher proton affinities for the *exo*-2-norbornyl chlorides are of particular interest. The origin of the differences is found to involve both stereoelectronic and steric effects. Implications concerning the solvolyses of the chlorides are considered briefly. The results for protonated **9** argue against the likelihood of a symmetric tight ion pair as an intermediate in the acetolysis of **9**.

Geometries and Relative Energies. The geometries calculated using MINDO/3 with complete geometry optimization for

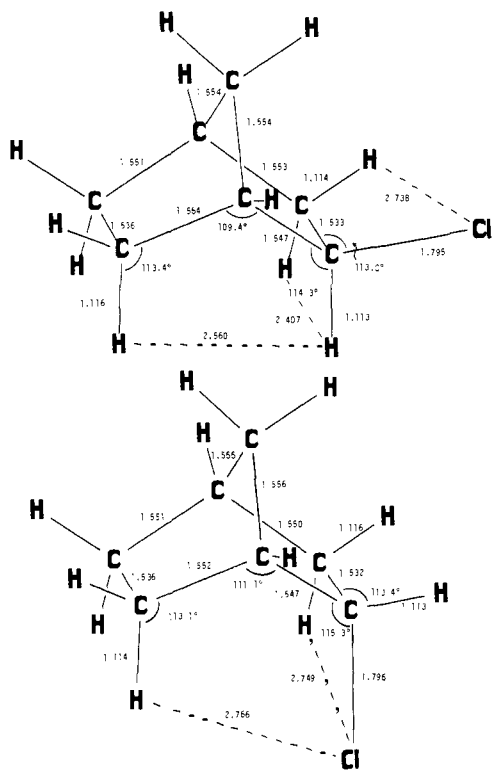


Figure 1. Important structural parameters computed for *exo*- and *endo*-2-norbornyl chloride.

9–12 are illustrated in Figures 1 and 2.^{13,14} The structures for the secondary species, **9** and **10**, are very similar. There is little evidence for increased strain in the endo form as the C(6)–C(1)–C(2) and C(1)–C(2)–Cl angles in **10** are $<2^\circ$ greater than the corresponding angles in **9**. The C(1)–C(6) and C–Cl distances are also notably constant, so there appears to be no strong interaction between the $\sigma_{C(1)-C(6)}$ and $\sigma^*_{C(2)-Cl}$ bond orbitals in **9**. Thus, it is not surprising that **10** is calculated to be only 0.2 kcal/mol higher in energy than **9**. The computed heats of formation are recorded in Table I.¹⁵ No experimental measure of the energy difference between **9** and **10** has been reported. However, Goering and Schewene¹⁶ determined the endo form of the secondary acetate to be 1.2 kcal/mol less stable than the *exo*. The reduced value for the chlorides is consistent with the smaller axial/equatorial preference for cyclohexyl chloride (0.52 kcal/mol) vs. cyclohexyl acetate (0.71 kcal/mol).^{17a}

The tertiary derivatives, **11** and **12**, show greater structural variation. The methyl group in **11** is clearly being pushed out of the endo cavity, while the chlorine in **12** is being pushed in. These effects may be attributed to the greater steric bulk of a methyl group compared with chlorine which is also reflected in the increased axial/equatorial preference for methylcy-

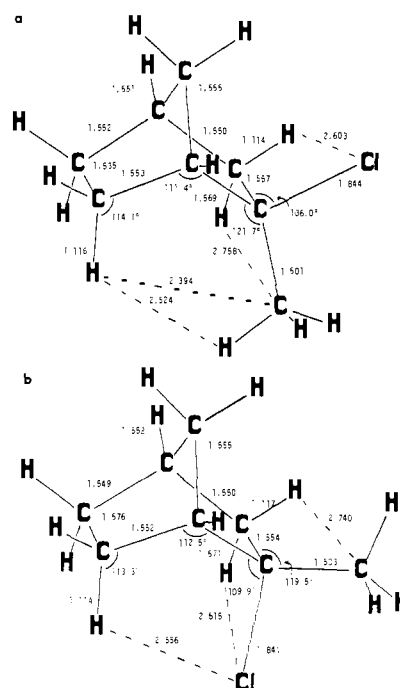
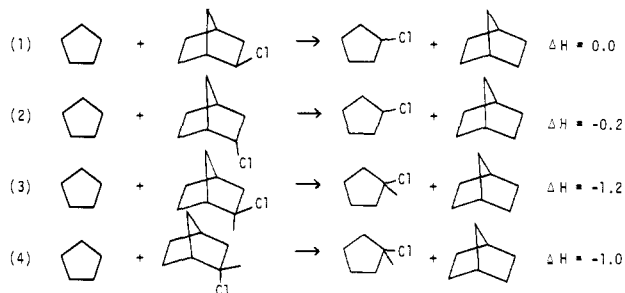


Figure 2. (a) Important structural parameters computed for 2-methyl-*exo*-2-norbornyl chloride (**11**). (b) Important structural parameters computed for 2-methyl-*endo*-2-norbornyl chloride (**12**).

clohexane (1.74 kcal/mol).^{17a} Consequently the *exo* epimer, **11**, is now calculated to be less stable than **12** by a small margin, 0.2 kcal/mol (Table I). The present results are also consistent with molecular mechanics calculations by Schleyer et al.^{17b} Using this approach, *exo*-2-methylnorbornane is computed to be 0.86 kcal/mol more stable than the endo isomer, while 2-methyl-*exo*-2-norbornanol is predicted to be 0.31 kcal/mol less stable than its endo analogue.^{17b}

The strain energy in **9–12** can be evaluated with reference to cyclopentyl analogues using isodesmic reactions. The computed ΔH_s for eq 1–4 indicate that **9** and **10** suffer from



essentially no more strain than cyclopentyl chloride, while **11** and **12** possess ~ 1 kcal/mol additional strain.¹⁸ Considering the reliability of MINDO/3 calculations and the nature of the

Table I. Calculated Properties for Chlorides^{a,b}

Chloride	ΔH_f	IP	ϵ_L	PA	ΔE_s^c	f_{CCl}	μ, D
<i>exo</i> -2-Norbornyl	0.0	10.22	0.34	193.2	18.9	3.49	2.21
<i>endo</i> -2-Norbornyl	0.2	10.29	0.35	189.3	14.7	3.65	2.17
2-Methyl- <i>exo</i> -2-norbornyl	1.7	10.05	0.24	203.1	8.8		2.31
2-Methyl- <i>endo</i> -2-norbornyl	1.5	10.16	0.23	198.5	4.5		2.24
Isopropyl	-34.2	10.74	0.32	191.2	21.0	3.16	2.17
Cyclopentyl	-35.3	10.48	0.34	191.1	20.9	3.00	2.14
<i>tert</i> -Butyl	-31.9	10.51	0.18	199.1	13.2	2.83 ^d	2.31
1-Methylcyclopentyl	-34.8	10.37	0.22	201.0	11.5		2.26

^a MINDO/3 results with complete geometry optimization. ^b Heats of formation (ΔH_f), proton affinities (PA), and ΔE_s in kilocalories/mole. Ionization potentials (IP) and LUMO energies (ϵ_L) in eV. C–Cl stretching force constants (f_{CCl}) in millidyne/angstrom. ^c ΔE_s is the ΔH for $RCIH^+ \rightarrow R^+ + HCl$. ^d D. G. Graczyk, R. L. Julian, J. W. Taylor, and S. D. Worley, *J. Am. Chem. Soc.*, **97**, 7380 (1975).

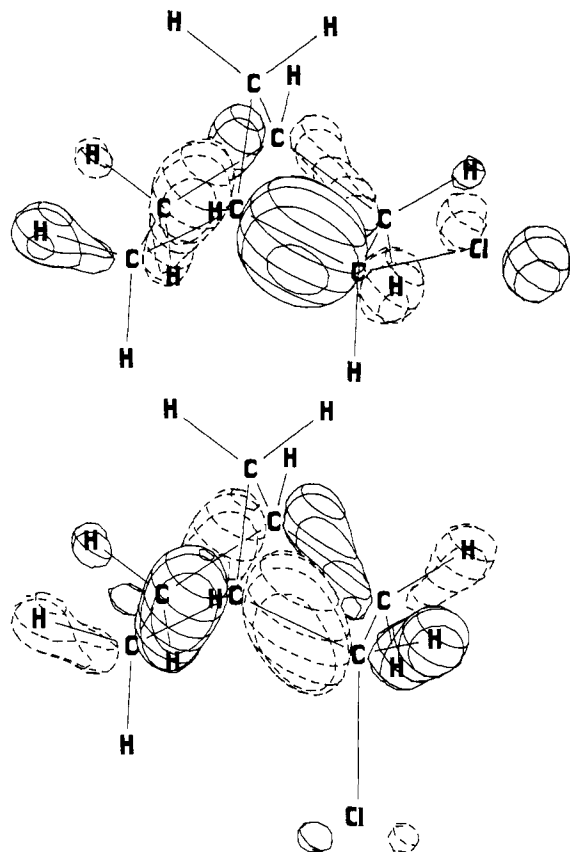


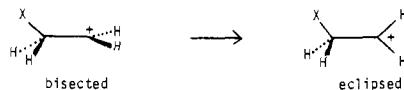
Figure 3. The HOMOs of *exo*- and *endo*-2-norbornyl chloride. The MOs are perturbed versions of the AA ribbon orbital of boat cyclohexane.

isodesmic relations, the results primarily reveal that there are no unusual, pronounced steric effects in the ground states of 9–12.

Ionization Potentials and Force Constants. The computed ionization potentials and LUMO energies for 9–12 are shown in Table I. The ionization potentials for the *exo* isomers are ~ 0.1 eV lower than for the *endo* species. This is intriguing since it reproduces the trend found by Kochi et al. for 1 and 2.⁶

A logical start for the analysis of the differences in the IPs is to draw the HOMOs of 9 and 10. The appropriate illustrations are presented in Figure 3.^{19,20} The HOMOs are seen to be simply perturbed forms of the HOMO of norbornane or boat cyclohexane which has been termed the “AA ribbon orbital” by Hoffmann et al.²¹ This latter MO is shown in Figure 4. The ribbon orbitals of chair cyclohexane have previously been illustrated.²²

The higher energy of the HOMO of 9 may be due to the replacement of the C(2)–H σ -bonding component in the HOMO of 10 (or boat cyclohexane) with the C(2)–Cl component, since this is the most obvious difference between the MOs in Figure 3. This would require that a σ_{C-Cl} bond orbital has higher energy or is more labile than a σ_{C-H} orbital. One way to test this is to compare the rotational barriers in the classical ethyl cation and the 2-chloroethyl cation. Following



the example of Hoffmann et al. a higher energy σ_{C-X} component will favor the bisected form while there is essentially no preference for $X = H$.²³ The barriers calculated by MINDO/3 for $X = F, H,$ and Cl are $-3.1, 0.62,$ and $+5.4$ kcal/mol, respectively, when the $X-C(2)-C(1)$ angle is restricted to 109.5° . Qualitatively similar results have been obtained by Clark using ab initio calculations.²⁴ Thus, the higher energy of the HOMO

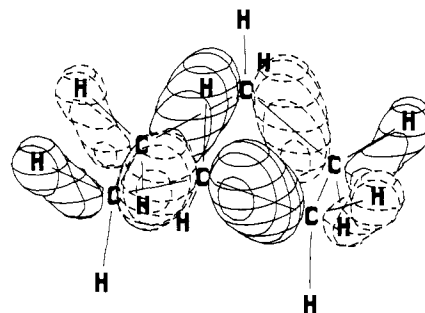


Figure 4. The AA ribbon orbital that is the HOMO of boat cyclohexane.

of 9 can be ascribed to the increase in C–Cl bonding and decrease in C–H bonding in the MO as compared with the HOMO of 10. Analogous reasoning can be used to help explain the lower IP for 11 than 12 since the computed barrier for $X = CH_3$ is still 2.2 kcal/mol lower than for $X = Cl$. The same conclusions may be obtained by simply noting that the order of bond strengths is $C-Cl < C-C < C-H < C-F$.²⁵

The next question is: are these results related to Kochi's findings for 1 and 2?⁶ The answer appears to be no. Work by Fehlner, Kochi, and others argues that the ionizations for 1 and 2 occur from HOMOs with a substantial C(2)–H component in both cases.²⁶ The HOMO for 2 would certainly bear little resemblance to the HOMO of 10 under these circumstances. Therefore, the origin of the lower HOMO energy for 2 must come from a different stereoelectronic source than for the comparison of 9 and 10.

It has been shown above that the lower IPs for the *exo*-2-norbornyl chlorides may be easily traced to the composition of the molecules' HOMOs. This does not signify that an *exo*-2-norbornyl substituent is a better electron donor than the *endo* alternative, particularly since the IP order would probably be reversed for fluorides. This substituent dependence clouds the claim of Kochi et al. that the photoelectron data on 1 and 2 are evidence of “enhanced σ participation” for an *exo*-2-norbornyl group.²⁷

The C–Cl stretching force constants calculated for 9 and 10 are given in Table I. The much higher values for 9 and 10 than for cyclopentyl chloride are due to the greater strain in the bicyclic framework which stiffens the external bonds. The effect is undoubtedly overestimated by MINDO/3.¹⁵ The most interesting result is the significantly lower force constant for the *exo* chloride than for the *endo*. Although this is consistent with the faster solvolyses of *exo* derivatives,³ force constants and solvolysis rates seem quite far removed. A possible link may be rate determining formation of ion pairs. This notion is considered further in a following section.

The lower force constant for 9 is a reasonable consequence of some details of the electronic structures for 9 and 10 that have just been discussed. First, since the HOMOs of 9 and 10 (Figure 3) indicate that 9 has higher energy C–Cl bonding components than 10, it requires less energy to modify the C–Cl bonding in 9. Also, a distortion causes remixing of the occupied and unoccupied MOs for a molecule, which is most pronounced for the frontier orbitals, the HOMOs, and LUMOs.²⁸ The LUMOs for 9 and 10 both have σ^*_{C-Cl} character and are isoenergetic (Table I). The smaller HOMO–LUMO gap and the increased concentration of the MOs in the CCl region for 9 should cause the mixing on C–Cl distortion to be more stabilizing for 9 than 10. Consequently, this would yield the lower CCl force constant for the *exo* isomer.

Protonated 2-Norbornyl Chlorides. Another property that is a good candidate for stereoelectronic effects is proton affinities. To test this idea, the protonated forms of 9–12 have been studied using MINDO/3 with complete geometry opti-

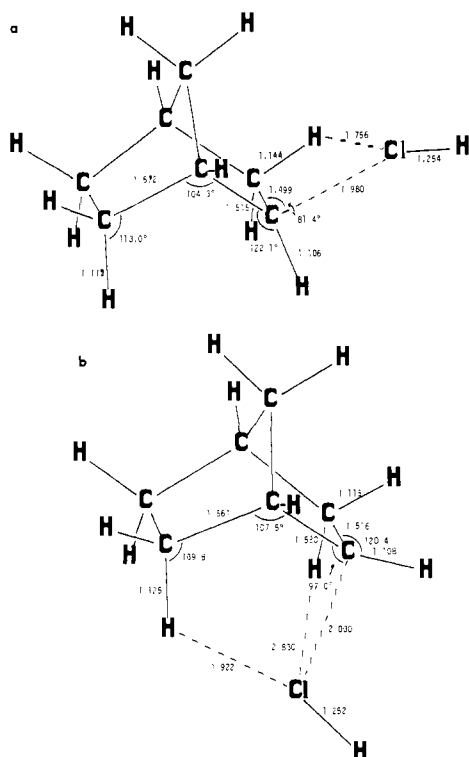


Figure 5. (a) Important structural parameters computed for protonated *exo*-2-norbornyl chloride (9). (b) Important structural parameters computed for protonated *endo*-2-norbornyl chloride (10).

mization. The resulting structures are shown in Figures 5 and 6. Two energetic quantities that may then be determined are the proton affinities (eq 5) and the energy, ΔE_s , required to separate a protonated species to the corresponding carbonium ion and HCl (eq 6). The computed values are given in Table I.

$$(5) \quad PA = \Delta H_f(RCl) + \Delta H_f(H^+) - \Delta H_f(RClH^+)$$

$$(6) \quad \Delta E_s = \Delta H_f(R^+) + \Delta H_f(HCl) - \Delta H_f(RClH^+)$$

For the secondary and tertiary chlorides, the PAs and ΔE_s are found to be ~ 4 kcal/mol higher for the *exo* isomers. The ΔE_s values suggest that a reasonable way to regard the protonated chlorides is as a fairly weak complex between the carbonium ions and HCl.^{2,29} As noted previously, comparisons with experimental data indicate that the computed PAs and ΔE_s are uniformly 6–7 kcal/mol too high.^{2,29} In turn, this implies that it is unlikely that the protonated tertiary norbornyl chlorides are bound, particularly at elevated temperatures that may be employed in mass spectrometry. That is protonated **11** and **12** would fall apart to 2-methyl-2-norbornyl cation and HCl. Rearrangements to more stable carbonium ions may also complicate protonation experiments for the secondary chlorides.

In view of the similar energies for the *exo* and *endo* isomers, **9**–**12**, the origin of the discrepancies in the PAs and ΔE_s can be sought in differences in the interactions of HCl with the *exo* and *endo* faces of the 2-norbornyl cations. A less stabilizing interaction raises the ΔH_f for the protonated chlorides and lowers the PA and ΔE_s (eq 5 and 6). The key interaction is again the mixing of the lone pair HOMO of HCl with the LUMO of the carbonium ions.^{2,29,30} Comparisons with cyclopentyl analogues are revealing. First, it should be noted that, according to MINDO/3, the *classical* norbornyl cations are both stabilized by roughly 4 kcal/mol compared with cyclopentyl cations (eq 7–8).³¹ The reason for the enhanced stability

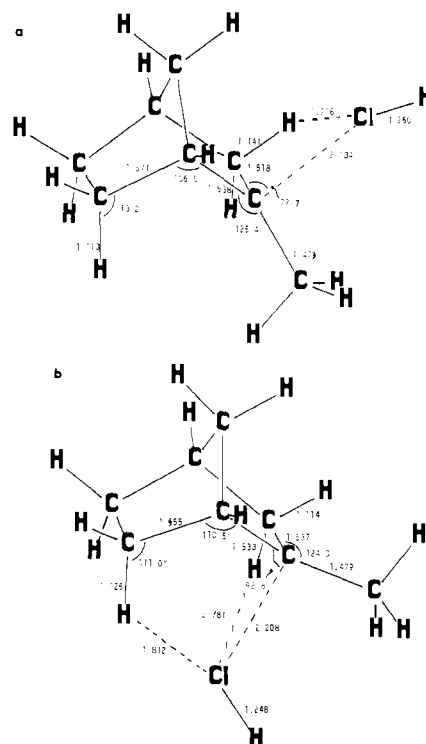
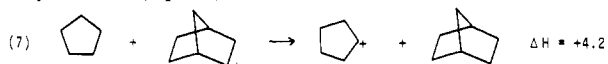


Figure 6. (a) Important structural parameters computed for protonated 2-methyl-*exo*-2-norbornyl chloride (11). (b) Important structural parameters computed for protonated 2-methyl-*endo*-2-norbornyl chloride (12).

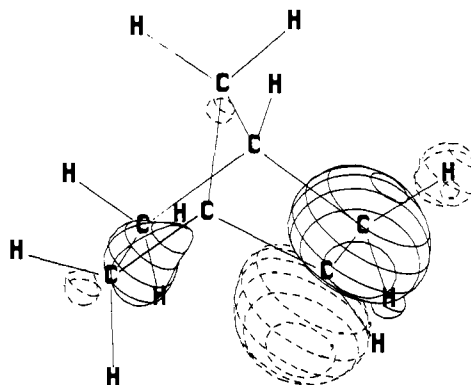
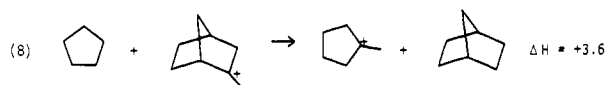
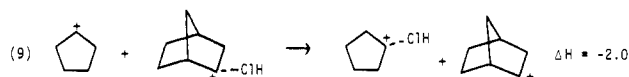


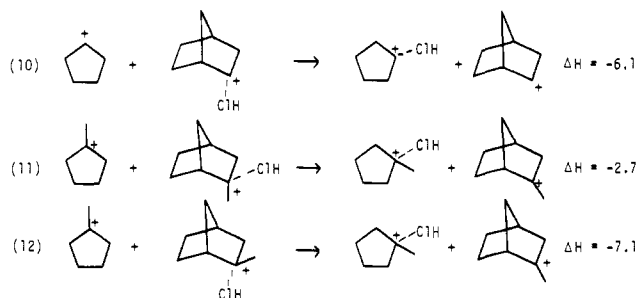
Figure 7. The LUMO of the 2-norbornyl cation.



is a strong interaction between the C(1)–C(6) σ -bond orbital and the empty 2p orbital on C(2) in the 2-norbornyl cation. This is due to the strain in the C(1)–C(6) bond and the excellent alignment of the bond and the empty 2p orbital. The interaction is clearly apparent in the striking contribution of the C(1)–C(6) bond orbital to the LUMO of the 2-norbornyl cation shown in Figure 7.³² As we have fully discussed in the past, out-of-phase contributions to the LUMOs of simple carbonium ions reflect hyperconjugation with the corresponding components.^{2,33}

The stabilities of the protonated chlorides are compared with cyclopentyl analogues in eq 9–12. The exothermicity of these

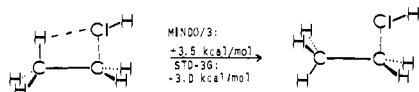




relations is due in part to the stability of the norbornyl cations (eq 7–8). However, the higher energies of the protonated endo chlorides are also caused by a combination of electronic and steric effects.

To begin, earlier MINDO/3 studies found that chlorines in protonated chlorides prefer coordination with both the carbonium carbon and a hyperconjugating hydrogen.^{2,29,30} As shown in the LUMO of the 2-norbornyl cation (Figure 7) this can be achieved on the exo face. Thus, the Cl–*exo*-3-H distance is short in protonated **9** and **11** (Figures 5a and 6a) and the corresponding MINDO/3 bond orders are +0.11 and +0.13, respectively. In contrast, on the endo face there is no strongly hyperconjugating hydrogen;³² so the interaction between the lone pair HOMO of HCl and the LUMO of the norbornyl cation is weaker. The interactions between chlorine and the endo-6-H in protonated **10** and **12** are found to be antibonding with bond orders of –0.01 (Figures 5b and 6b). The closeness of approach of the chlorine to the endo-6-H in these latter species is partially a consequence of attempting to maintain maximum overlap between the chlorine lone pair HOMO and the endo lobe of the empty 2p orbital on C(2) in the LUMO of the 2-norbornyl cation (Figure 7). Brown and Schleyer discussed the likelihood of a similar effect as the leaving group departs in the solvolyses of endo derivatives.³⁴ The effect is clearly enhanced in the tertiary species (Figures 5b and 6b), though the energetic consequence is only 1 kcal/mol (eq 10 and 12).

Although the preceding analysis accounts for the MINDO/3 predictions, it must be tempered by the fact that our ab initio studies² showed that the MINDO/3 method finds nonbonded interactions with chlorine too attractive. A key example is the erroneous favoring of the eclipsed rather than staggered rotamer of protonated ethyl chloride.² Under these circumstances it is reasonable to assume that the MINDO/3



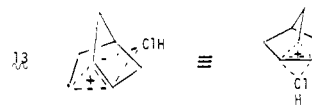
calculations are overestimating the attraction between chlorine and the *exo*-3-H in protonated **9** and **11**. Similarly, the repulsion between chlorine and the *endo*-6-H in protonated **10** and **12** is undoubtedly underestimated. Since the energetic errors are compensating and their magnitude is not great,² it is most likely that the qualitative conclusion that the *exo* chlorides have higher proton affinities and ΔE_s s is correct. However, little significance can be attached to the quantitative predictions. Furthermore, in the absence of unusual attractive effects such as the chlorine–*exo*-3-H interaction, lower PAs and ΔE_s s for the endo chlorides may reasonably be ascribed to steric effects in the endo cavity along the lines of the suggestion by Brown and Schleyer.³⁴

Model Ion Pairs and Solvolysis Rates. In discussing the solvolyses of simple secondary substrates under conditions such as acetolysis, it is important to keep in mind that ion pairs are formed and not free carbonium ions.³⁵ In other publications, we have stressed the utility of protonated alkyl chlorides as models for tight ion pairs.^{2,29} In the present context, it seemed reasonable to search for a symmetric “ion pair” (**13**) which

Table II. Relative Solvolysis Rates and Proton Affinities

Tosylate	Log k_{rel}^a	ΔPA (RCI) ^b
<i>endo</i> -2-Norbornyl	0.0	0.0
Cyclopentyl	1.4	1.8
Isopropyl	0.0	1.9
<i>exo</i> -2-Norbornyl	2.6	3.9
2-Methyl- <i>endo</i> -2-norbornyl	6.7	9.2
<i>tert</i> -Butyl	7.6	9.8
1-Methylcyclopentyl	9.0	11.7
2-Methyl- <i>exo</i> -2-norbornyl	9.7	13.8

^a Experimental values for acetolysis at 25 °C. The rates for the tertiaries have been converted from data on OPNBs in 80% acetone. See ref 2a, footnote 41, for details. ^b MINDO/3 results in kilocalories/mole from Table I.



corresponds to HCl interacting with the nonclassical 2-norbornyl cation. Since the species is not a minimum according to MINDO/3, its energy could only be determined by enforcing a plane of symmetry in the calculations. The result is that **13** is found to be 16.0 kcal/mol higher in energy than protonated **9** (Figure 5a). It is also unlikely that **13** would be bound since the computed dissociation energy, ΔE_s , is only 4.7 kcal/mol. Naturally, if the MINDO/3 energy difference between the classical and nonclassical 2-norbornyl cations (1.9 kcal/mol)¹³ overly favors the classical ion by a far margin, the conclusions for the model ion pairs could reverse. This seems doubtful for two reasons. First, as Dewar discusses, if MINDO/3 has a general tendency, it is to somewhat overestimate the stability of nonclassical ions.^{12,37} Secondly, as we have belabored, nonclassical ions interact less strongly with HCl and are subject to diminished substituent effects as compared with classical isomers owing to the higher energy and greater delocalization of their LUMOs.^{2,29,30,36} The possibility that additional solvation might reverse the trend also appears remote based on our study of the solvation of bisected and bridged ethyl cations³⁰ and other discussions.^{2,29}

Thus, it is reasonable to conclude that the generation of a symmetric tight ion pair from *exo*-2-norbornyl chloride as an intermediate under acetolysis conditions is unlikely. Furthermore, it seems even less probable that the high *exo*/*endo* rate ratios for the acetolyses of 2-norbornyl substrates could be due to the attainment of bridging in a symmetric ion pair reminiscent of **13**. Under conditions where the interactions of the solvent and counterion with the incipient carbonium ion are much weaker as in superacid, it is still possible that the 2-norbornyl cation is bridged.³¹

Our intention here was not to explain the *exo*/*endo* rate ratios for solvolyses, but rather to probe stereoelectronic effects on the properties of 2-norbornyl chlorides. However, it is difficult to resist pointing out that there is a rough correlation between solvolysis rates and proton affinities for alkyl chlorides (Table II).² Thus, it is conceivable that some of the stereoelectronic factors and steric effects that have been found here to control the differences in proton affinities, C–Cl stretching force constants, and ionization potentials for *exo*- and *endo*-2-norbornyl chlorides may prove useful in clarifying the lengthy debate on the origin of the *exo*/*endo* rate ratios. Furthermore, we are not unaware of the similarity of the present results in spite of their quantitative limitations and the Goering–Schewene diagram,^{3,16,34} since the ground states of **9** and **10** are found to be separated by 0.2 kcal/mol and their protonated forms to differ by 4.1 kcal/mol.

In conclusion, it is clear that the chemical behavior of molecules containing the norbornyl framework will continue to

provide a rich source of intriguing problems. Hopefully, the present work establishes that the fascination extends beyond competing transition states to the physical properties of norbornyl derivatives in their ground states.

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- (13) The drawings of structures and molecular orbitals were made using the PSI/77 program written by W. L. Jorgensen. The program is available from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47401, program no. 340.
- (14) Complete geometric parameters calculated for the molecules in this work may be obtained from the authors upon request.
- (15) The MINDO/3 values for the heats of formation of norbornyl compounds are uniformly too high by ~ 20 kcal/mol.⁹
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- methylcyclopentyl cation (164.3 kcal/mol), 1-methylcyclopentyl chloride (-34.8 kcal/mol), and its protonated form (131.2 kcal/mol). Some of the values differ from Dewar's earlier reports,⁹ presumably owing to improvements in the current MINDO/3 optimization procedures.
- (19) The drawings of the MOs were constructed in the usual way¹³ using EH wavefunctions and the MINDO/3 geometries.
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- (32) The larger coefficient on the *exo*-3-H compared to the *endo*-3-H indicates stronger hyperconjugation with the former hydrogen. This is consistent with the more facile *exo* 3 \rightarrow 2 hydride shifts observed experimentally and theoretically for 2-norbornyl cations.^{3,4,12}
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- (37) NOTE ADDED IN PROOF. Additional support can be found for the description of the 2-norbornyl cation by MINDO/3. Particularly, the agreement between the ΔH_f s in eq 7 and 8 and Arnett's recent work³¹ is good. In addition, the MINDO/3 value for the proton affinity of norbornene, 197.8 kcal/mol,³⁸ also compares well with the ICR value, 198.8 kcal/mol.³⁹ Thus, it appears that the strain in norbornyl derivatives is uniformly overestimated by MINDO/3.⁹ However, the method's performance on the 7-norbornyl cation is still an anomaly⁴⁰ ($\Delta H_f = 211.1$ kcal/mol³⁸ vs. 214.2 kcal/mol for 2-norbornyl¹²).
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Molecular Asymmetry in *trans*-Thiacycloalkenes. 1. Interconversion of Diastereomeric *trans*-2-Methylthiacyclooct-4-enes

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Abstract: Rearrangement of the allyl sulfonium ylide derived from *cis*- and *trans*-1-ethyl-2-vinylthiolanium hexafluorophosphate gives three ring-expanded products, *cis*-2-methylthiacyclooct-4-ene (**2**) and two diastereomeric *trans*-2-methylthiacyclooct-4-enes, **3** and **4**. The existence of the latter two is evidence of the molecule possessing two elements of chirality, a chiral center (C_2) and a plane, the diastereoisomers deriving their stability from restricted conformational inversion around the chiral plane. The two diastereoisomers are capable of thermal interconversion in what appears to be a purely unimolecular process ($\Delta H^\ddagger = 29.7$ kcal/mol, $\Delta S^\ddagger = -1$ eu) similar to that responsible for the racemization of *trans*-cyclooctene,⁴ but considerably faster (a factor of 10^3). The greater ease of stereomutation of the heterocyclic olefin is discussed in relation to the conformational processes required for inversion around the chiral plane.

Medium- and large-size carbocycles ($n \geq 8$) may incorporate a *trans* double bond. The resulting species are dissymmetric and give rise to enantiomeric conformations,¹ whose stability

appears to depend on ring size. For the larger rings ($n \geq 10$) the enantiomeric conformers interconvert rapidly at room temperature and cannot be separated;² however, the rates of