C1 and C2. The preferential attack on hydrocarbon **1** by the nucleophile at C2 as compared to C1 (62:38) clearly demonstrates that protonated intermediate **4b** must be trapped by the nucleophile at least to the extent of 24% before conversion to the symmetrical species **5b**.[11]

The observation of mercuric ion cleavage of the most substituted cyclopropane bond in this study is in direct conflict with previously stated rules for mercuric ion induced cyclopropane ring opening[12] and is in contrast to an earlier prediction[13] of the regioselectivity of this reaction. The unsymmetrical mercurated cation **4c** unlike the deuteriated analogue **4b** does not rearrange to the more symmetrical corner-protonated cation **5c**. Apparently a high degree of orbital interaction between C4 and C2 in the cation **4c** results in little charge development at C2. This reaction is therefore formally similar to that of alkenes with mercuric acetate[12] where skeletal rearrangement is not normally observed.

The favorable attack by the electrophiles deuteron and mercuric ion at the corner of the cyclopropane ring reflects the favorable interaction of both the degenerate HOMO's of the cyclopropane with the H 1s and d$_\sigma$LUMO of the electrophile, respectively (Chart I (part a)). It should be noted for edge attack that while the HOMO/LUMO interaction is favorable for proton interaction with the symmetric Walsh orbital this is not the case with the unsymmetric orbital (Chart I (part b)). The preference for corner attack reflects the favorable HOMO/LUMO interaction for both degenerate molecular orbitals. A favorable interaction of the LUMO Walsh orbitals of cyclopropane with the d-orbitals of electron donor metals allows oxidative addition[14] at the edge of the cyclopropane (Chart II). This interaction compensates for the more favored σ-interaction at the corner of cyclopropane between the HOMO Walsh orbitals and the LUMO orbitals of the electrophile. For mercury the donor ability[15] of the d$_\pi$-orbitals is small and thus the d$_\pi$HOMO, cyclopropane LUMO interaction is unimportant, and the reaction stereochemistry parallels the reaction with deuteron.[16]

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(10) A small isotope effect will perturb the symmetry of this cation as represented. A functionally equivalent representation of symmetrical corner-protonated cation **5b** as two rapidly equilibrating unsymmetrical corner-protonated cations may also be considered for this intermediate.

(11) The stability of methoxy ether **2** to the reaction conditions was established by heating a sample of 3,3,4-*exo*-trideuterio-2-*endo*-methoxybicyclo[3.2.1]octane (cf. Scheme II) with *p*-toluenesulfonic acid for 7 days. The absence of rearrangement in the recovered starting material (^{13}C NMR) confirms the kinetic origin of the **2b**:**3b** ratio observed in the reaction of hydrocarbon **1** with acid in methanol-d_1.

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(16) (a) The generality of this conceptualized molecular orbital approach to the stereodifferentiation of electrophilic attack on cyclopropane is substantially upheld by a detailed examination of orbital interactions in hydrocarbon **1** and related systems (manuscript in preparation). (b) A prevalent opinion persisting in the area of acid-catalyzed ring opening of cyclopropanes is nicely summarized by the following referees observation: "...experiment and theory agree that the difference in energy between corner and edge protonated cyclopropanes is quite small. Therefore, the cited HOMO/LUMO interaction cannot contribute much. And, it is known from earlier studies that many of the cyclopropane orbitals are strongly perturbed on protonation—not just the HOMO." It is precisely these conclusions that the present experimental results, along with the theoretical calculations of Wiberg and Kass, call into question. Prior to the latter work the mechanistic role of the unsymmetrical corner-protonated cyclopropane had not been properly recognized. In particular, the optimized structures calculated for such unsymmetrical cations derived from methyl-substituted cyclopropanes are convincingly lower in energy than either the edge protonated or any of the symmetrical corner-protonated structures.[1a,d] No calculations have as yet been carried out on the unsymmetrical cation **4a**, but these results and our arguments in ref 1c suggest it is a reasonable intermediate not only for this system but also for cyclopropane itself.

Evidence for a Selenium Anomeric Effect? An Unusual Conformation of a Selenium Coronand

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The anomeric effect[1] has been the subject of intense investigation by both experimental and theoretical chemists alike.[2] While the existence of this conformational effect in X–C–Y systems containing first-row atoms has been widely accepted, the existence of significant anomeric interactions involving second- and lower-row atoms has been questioned recently.[3,4] We present herein unprecedented evidence for the existence of a third-row anomeric effect, based on an unusual solid-state conformation adopted by a selenium coronand.

In its generalized form, the anomeric effect refers to the torsional preferences about the C–X and C–Y bonds in RXCH$_2$YR′ molecules. The conformations increase in energy in the sequence gauche, gauche **1** < anti, gauche **2** < anti, anti **3** (Figure 1). The torsional behavior, bond length variations, and bond angle variations in RXCH$_2$YR′ have been rationalized both qualitatively[2,5] and quantitatively[6] by a perturbational molecular orbital (PMO) treatment that focuses on the stabilizing orbital interactions between the p-type nonbonding orbitals on X and Y, n_X and n_Y, with the acceptor orbitals, σ^*_{C-Y} and $\sigma^*_{C-X'}$ respectively. Whereas both these interactions may be expressed in **1**, symmetry considerations dictate that only the n_X–σ^*_{C-Y} is possible in **2** and neither interaction is possible in **3**. These hyperconjugative interactions account for the existence of the endo and exo anomeric effect[7,8] when the RXCH$_2$YR′ moiety is incorporated into a heterocyclohexane (Figure 1).

X-ray crystallographic analysis[9] of the selenium coronand, 1,3,7,9,13,15-hexaselenacyclooctadecane (**4**),[10] reveals that the ring has a very unusual irregular geometry, in sharp contrast to the regular quadrangular shapes normally exhibited by even-membered cycloalkane derivatives.[11] The two long sides of this elongated ring, shown in Figure 2, are distinctly different in

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(9) $Se_6C_{12}H_{24}$: monoclinic, $P2_1/c$; T = 190 K; a = 20.154 (3) Å, b = 5.4292 (9) Å, c = 17.678 (3) Å, β = 110.66 (1)°; Z = 4; λ = 0.71069 Å; μ (Mo Kα) = 120.0 cm^{-1}; crystal dimensions 0.10 × 0.55 × 0.21 mm; transmission 0.083–0.330, corrected analytically; 2θ: 2–52°; data $I \geq 2.5\sigma(I)$, 2426; refined parameters, 163; $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ = 0.024; maximum |shift/error| < 0.01; bond distances: Se–C 1.932 (6)–1.967 (6) Å, C–C 1.501 (9)–1.530 (9) Å; bond angles: C–Se–C 94.3 (3)–100.4 (3)°, Se–C–Se 116.0 (3)–118.6 (3)°, C–C–Se 108.9 (4)–116.6 (5)°, C–C–C 111.8 (4)–115.8 (5)°.

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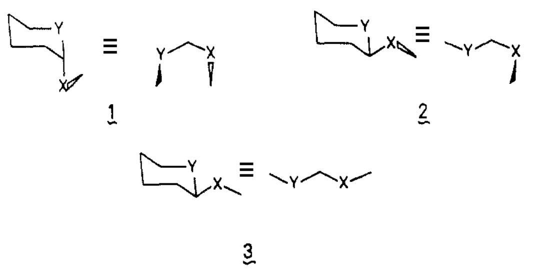

Figure 1. Conformations of $RXCH_2YR'$ molecules and their relationships to the conformations of 2-substituted heterocyclohexanes.

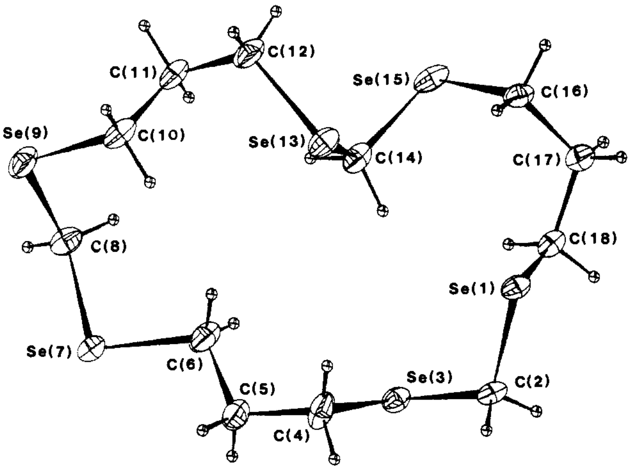

Figure 2. Molecular structure of **4**.

character. The lower side of the ring, as shown, displays features usually characteristic of medium-sized macrocycles[11] in that it is made up of planar atomic sequences consisting of one or two anti torsion angles joined at "corners" formed by one or two gauche torsion angles. The upper side of the ring displays the unusual feature of an eight-atom helix, from C(10) to C(17), resulting from five consecutive gauche torsion angles of the same sign. The two sides are connected at the "corner" atom C(17) and by Se(9). Se(1), Se(3), and Se(13) can be described as endodentate while Se(7), Se(9), and Se(15) are exodentate. The sequence of torsion angles about the ring, beginning at the Se(1)–C(2) bond, may be represented as G^- G^- A G^- A A G^- G^+ G^+ A G^+ G^+ G^+ G^+ G^+ G^- G^- A.

The conformation of **4** is best analyzed in terms of the preferred torsion angles for the different four-atom sequences, Se–C–C–C, C–Se–C–C, and Se–C–Se–C. For $[CH_2CH_2E]_n$ (E = S, O), where anomeric interactions are not possible, gauche torsion angles are found preferentially about C–S bonds but not about C–O bonds.[12] It has been suggested,[12] based on a consideration of 1,4-interactions, that gauche preferences about C–X bonds should decrease in the order C–S $\gg$ C–C > C–O primarily as a consequence of the longer C–S bond. Similarly, we find that the gauche torsion angles of **4** are found preferentially about C–Se bonds. More importantly, however, gauche torsion angles are displayed by six out of six Se–C bonds in the Se–C–Se–C sequences but only by three out of six Se–C bonds in the C–Se–C–C sequences. The marked preference by the former is striking evidence for the existence of a selenium anomeric effect, which thus appears to be the dominant influence on the overall molecular conformation.[13] A strong preference for gauche, gauche arrangements in C–O–C–O–C fragments has been noted in oxygen coronands containing 1,3-dioxa groupings.[14] Se–C bond lengths in the Se–C–Se (gauche, gauche) fragments of **4** are not significantly different from those in anti, gauche arrangements displayed by 1,3,7,9-tetraselenacyclododecane.[10] Two unimposed intermolecular Se–Se contacts might contribute to stabilizing the molecular conformation of **4**.[15]

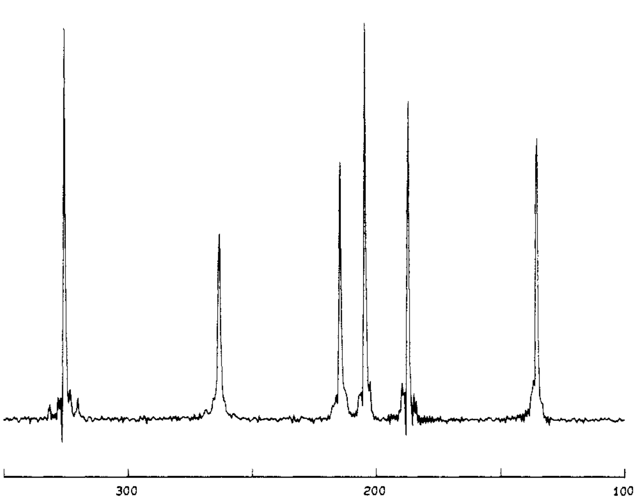

Figure 3. Solid-state CP-MAS ^{77}Se NMR spectrum of **4**.

The solid-state CP-MAS ^{77}Se NMR spectrum of **4** (Figure 3) displays six peaks of equal area.[16] The two resonances at lowest field have been assigned to Se(7) (326.5 ppm) and Se(9) (264.3 ppm) based on the following: (1) their relatively large mutual spin–spin coupling constant, $^2J_{^{77}Se-^{77}Se} = 128$ Hz, consistent with these atoms displaying the largest C–Se–C and Se–C–Se bond angles in the molecule; the evidence implies maximal s-orbital character in the connecting bonds; and (2) the broader line width of the resonance at 264.3 ppm indicative of more rapid relaxation associated with the greater average thermal motion of Se(9).[17] Point 1 is of significance since expression of the anomeric effect is predicted to open up the X–C–Y bond angle.[2g] Apparently the Se–C–Se anomeric effect is maximized in the Se(7)–C(8)–Se(9) fragment relative to the other two similar units. It is interesting to note that the largest gauche torsion angle (94.4 (4)°) is found in the former unit, a result that has implications for the optimum geometry[6] required for expression of n_{Se}–σ^*_{C-Se} anomeric interactions.

The solid-state ^{13}C CP-MAS NMR spectrum displays nine resolved peaks of relative areas 1:3:1:2:1:1:1:1:1.[16] Previous work[10,18] suggests the assignment of the three highest field peaks to the three methylene carbon atoms of the Se–C–Se moieties.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Solid-state CP-MAS ^{13}C NMR spectrum, details of the structure determination, tables of atomic coordinates with equivalent isotropic thermal parameters for C and Se and assigned coordinates and isotropic thermal parameters for H, anisotropic thermal parameters for C and Se, bond lengths and bond angles, and torsion angles for **4** (8 pages); table of calculated and observed structure factors for **4** (16 pages). Ordering information is given on any current masthead page.

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(15) Se(7)–Se(9)′ 3.6228 (12) Å, ′ = 1 − x, $y - {}^1/_2$, ${}^1/_2 - z$; Se(7)–Se(9)″ 3.7994 (12) Å, ″ = 1 − x, $y + {}^1/_2$, ${}^1/_2 - z$. Attempts to confirm the molecular conformation in solution by ^{77}Se and ^1H NMR spectroscopy at 145 K were unsuccessful because of rapid site-exchange. We note, however, that the average chemical shift of the ^{77}Se NMR signals in the solid-state spectrum (δ 223 ppm) is similar to that (δ 206 ppm) in the solution spectrum at ambient temperature.

(16) CP-MAS $\delta_{^{77}Se}$ (±1 ppm; ref Me_2Se): 136 ($w_{1/2}$ = 16 Hz), 188 ($w_{1/2}$ = 13 Hz), 206 ($w_{1/2}$ = 14 Hz), 216 ($w_{1/2}$ = 18 Hz), 264 ($w_{1/2}$ = 25 Hz), 327 ($w_{1/2}$ = 13 Hz). CP-MAS $\delta_{^{13}C}$ (±0.3 ppm; ref TMS): 16.0, 19.2, 20.2, 23.7, 25.7, 28.4 (rel intensity $\simeq$ 2), 29.7, 30.9 (rel intensity $\simeq$ 3), 33.9.

(17) Supplementary Material.

(18) Pinto, B. M.; Johnston, B. D.; Nagelkerke, R., manuscript in preparation.