Conformational Analysis of Selenanes and Telluranes

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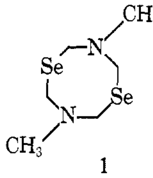
Abstract: The conformational properties of selenium and tellurium pentamethylene heterocycles have been examined. The free energy of activation to ring reversal for selenane is 8.2 kcal/mol; for selenane 1-oxide, 8.4 (axial to equatorial); for selenane 1,1-dioxide, 6.7; and for tellurane, 7.3. The barriers are found to correlate well with the torsional properties of the C–X bonds. As a result, some predictions can be made about unknown C–X torsional barriers. Angle strain is shown not to be an important contributor to the barrier height. At −130°, the nmr spectrum of selenane 1-oxide contains separate resonances for the equatorial (16%) and the axial (84%) isomers. The preponderance of the axial isomer is attributed to attractive 1,3 and 1,5 interactions. The coupling constant between the α protons in the *Se*-methyl salt of selenane indicates that the methyl group is almost entirely axial. Similar analysis of the *S*-methyl salt of thiane indicates that the methyl group is equatorial.

Although conformational analysis of ring systems was first directed toward alicyclic compounds, during the past 10 years an increasing proportion of studies has been concerned with heterocycles.[2] The bulk of this work has dealt with heterocycles containing the first-row elements nitrogen[3] and oxygen.[4] Very recently, interest has begun to grow in the conformational properties of heterocycles containing the second-row elements silicon,[5] phosphorus,[6] and sulfur.[4,7] Little or no conformational investigations have been carried out on heterocycles containing the "long-row" atoms germanium, tin, arsenic, antimony, selenium, and tellerium. We are involved in a conformational program in this area, and we report in the present paper our studies of heterocycles containing the long-row group VI atoms, selenium and tellurium.

The earliest study of the solution conformation of a selenium containing heterocycle was concerned with the barrier-to-ring reversal in the eight-membered ring **1**.[8] Soon thereafter, the introduction of the *R*-value method[9] permitted the determination of the shapes of 1,4-diselenane,[9] selenane (**2**), and tellurane (**3**)[10] in solution. In this same study,[10] an attempt was made to slow the process of ring reversal in **2** and **3**, but no spectral changes were observed down to −100°. The solution structures of the halogen adducts of selenane and tellurane have also been determined by the *R*-value method.[11] Analysis of vicinal coupling constants has shown that protonated selenane and tellurane exist exclusively in the form with the proton in the axial position.[10] In addition to this limited number of studies dealing with the solution conformations of selenium and tellurium heterocycles, X-ray crystallographic determinations have been reported on the solid-phase structure of some such molecules.[11]



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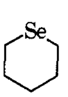

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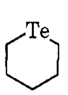

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The present paper deals with two aspects of the conformational analysis of these heterocycles, the kinetics of chair-chair interconversion and the preference of substituents on the heteroatom for the axial position. As noted above, previous attempts to observe ring reversal in selenanes and telluranes met with failure.[10] With instrumentation capable of going to lower temperatures, we have been able to slow down the process in selenane and tellurane and in the oxide and dioxide of the selenium system (**4**,**5**). The decrease in the barrier-to-ring reversal as the heteroatom descends group VI is confirmed by a redetermination of the barriers for the oxygen and sulfur heterocycles, tetrahydropyran and thiane.

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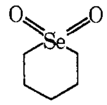

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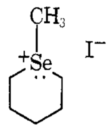

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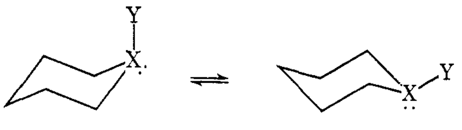
Substituents on trivalent heteroatoms may be either axial or equatorial (eq 1). The preference of some such substituents for the axial position was first recognized in



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(1) (a) This work was supported by the National Science Foundation (Grants GP-34259X and GP-35868X) and by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 2970-AC4); (b) National Science Foundation Trainee, 1968–1969; (c) National Institutes of Health Fellow, 1967–1971.

(2) (a) F. G. Riddell, *Quart. Rev., Chem. Soc.*, **21**, 364 (1967); (b) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965, Chapter 7.

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(5) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *Tetrahedron*, **27**, 3065 (1971); M. T. Tribble and N. L. Allinger, *ibid.*, **28**, 2147 (1972); R. J. Ouellette, D. Baron, J. Stolfo, A. Rosenblum, and B. Weber, *ibid.*, **28**, 2163 (1972).

(6) A. T. McPhail, P. A. Luhan, S. I. Featherman, and L. D. Quin, *J. Amer. Chem. Soc.*, **94**, 2126 (1972); J. B. Lambert and W. L. Oliver, Jr., *Tetrahedron*, 27, 4245 (1971); W. G. Bentrude and K. C. Yee, *J. Chem. Soc., Chem. Commun.*, 169 (1972).

(7) C. H. Bushweller, *Mech. React. Sulfur Compounds*, **5**, 75 (1970).

(8) J. M. Lehn and F. G. Riddell, *Chem. Commun.*, 803 (1966).

(9) J. B. Lambert, *J. Amer. Chem. Soc.*, **89**, 1836 (1967); J. B. Lambert, *Accounts Chem. Res.*, **4**, 87 (1971).

(10) J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Amer. Chem. Soc.*, **89**, 5921 (1967).

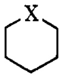
(11) (a) J. B. Lambert, D. H. Johnson, R. G. Keske, and C. E. Mixan, *ibid.*, **94**, 8172 (1972); (b) J. B. Lambert and R. G. Keske, *Tetrahedron Lett.*, 4755 (1967).

thiane 1-oxide (eq 1, S=O).[12] It has been suggested that the axial preference is due to attractive interactions between the 1 substituent in the axial position and the carbons and axial protons in the 3 and 5 positions.[13] The Morse-like potential function that describes the interaction between nonbonded atoms has a repulsive region at very short distances, an attractive region at intermediate distances, and little interaction at great distances. For each substituent Y in eq 1, there is an optical distance from the 3,5 atoms that gives rise to the most attractive interactions, and hence to the largest proportion of axial conformer. This distance can be controlled by changing the X atom, since a longer C–X bond length will alter the 1,3 and 1,5 interactions. Comparison of sulfur and selenium systems therefore permits a qualitative assessment of the nature of the potential well. If the sulfur systems do not represent the optimal geometry for attractive interactions, the longer bonds in the selenium compounds should increase the proportion of axial isomer in eq 1. On the other hand, if the sulfur system possesses the optimal geometry, the longer bonds will result in less attractive interactions and a decrease in the axial population. In this study we have compared the oxides (eq 1, S=O and Se=O) and the methyl "onium" salts ($^{+}S—CH_3$ and $^{+}Se—CH_3$) and found that for both substituents the selenium heterocycles have the larger proportion of axial isomer.[14]

Results

The 90-MHz proton spectra of selenane and tellurane, deuterated in the β positions, contain singlets for the α and γ protons at room temperature. Below −100°, these singlets pass over to AB quartets. The spectral parameters for these two compounds are collected in Table I. For the sake of comparison and because all pertinent parameters were not previously measured,[10] we obtained analogous data for pentamethylene oxide (tetrahydropyran) and thiane and include them in the table. Free energies of activation were calculated for all four compounds according to standard methods:[15] oxide (10.3 kcal/mol), sulfide (9.4), selenide (8.2), and telluride (7.3). In addition, a complete line-shape analysis was carried out for the spectral changes in the α-proton resonances of selenane: E_a = 11.2 kcal/mol, log A = 16.3, $\Delta H^{\ddagger}$ = 10.6 kcal/

Table I. Spectral Parameters for Group VI Pentamethylene Heterocycles[a]



	O	S	Se	Te
Solvent	$CD_3OD/CHClF_2$	$CD_3OD/CHClF_2$	$CHClF_2$	$CHClF_2/CHCl_2F$
T_c, °C[b]	−61	−81	−105	−119
$\delta_{ae}(\alpha)$[c]	0.50	0.187	0.295	0.75 ± 0.05[d]
$J_{ae}(\alpha)$[c]	11.2	13.6	12.3	11.0 ± 1.2[d]
$\delta_{ae}(\gamma)$[c]	0.32	0.50	0.47	0.68 ± 0.05[d]
$J_{ae}(\gamma)$[c]	13.2	13.9	13.9	13.0 ± 1.2[d]

[a] All samples were deuterated in the β positions, and spectra were taken at 90 MHz. [b] Coalescence temperatures for the α-proton resonances. [c] Chemical shift differences are in ppm and coupling constants in Hz. [d] Except as indicated, all figures are ±0.01 ppm or ±0.1 Hz; the tellurane data are less precise because of extremely broad peaks.

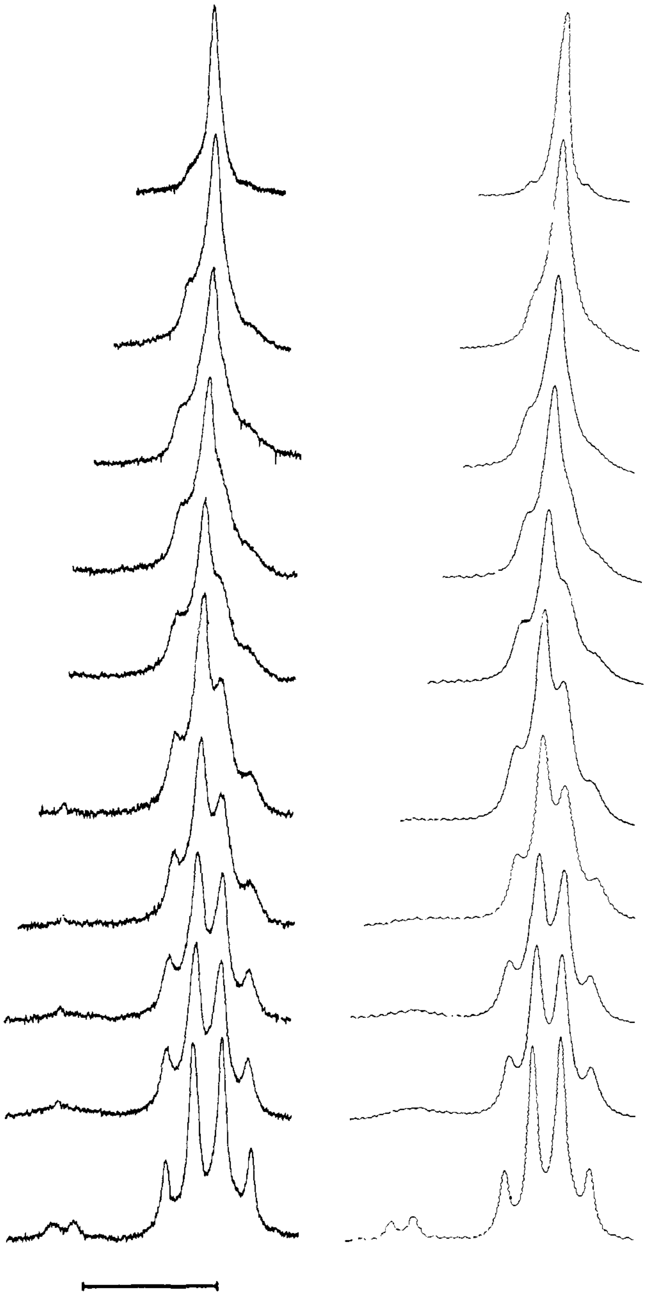


Figure 1. The observed (left) and calculated 90-MHz spectra of the α protons of selenane-*3,3,5,5-d*$_4$ 1-oxide (**4**) in $CHClF_2$ as a function of temperature. From top to bottom, the temperatures and the mean lifetimes (k^{-1}) for both isomers are: −79° (fast exchange), −98 (0.0105, 0.0020), −100 (0.015, 0.0029), −102 (0.021, 0.0040), −104 (0.029, 0.0055), −106 (0.039, 0.0074), −108 (0.049, 0.0093), −112.5 (0.080, 0.0152), −114.5 (0.091, 0.0173), and −130 (slow exchange). At −130°, peaks 3, 4, 5, and 6 correspond to the more populous axial isomer. Peaks 1 and 2 and a doublet directly under peaks 5 and 6 comprise the resonances for the equatorial isomer. There is a very small impurity peak at approximately the same position as peak 1. The calibration bar represents 60 Hz.

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[12] (a) C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **86**, 2935 (1964); (b) J. C. Martin and J. J. Uebel, *ibid.*, **86**, 2936 (1964); (c) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).

[13] N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, **91**, 337 (1969).

[14] J. B. Lambert, C. E. Mixan, and D. H. Johnson, *Tetrahedron Lett.*, 4335 (1972).

[15] G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

mol, $\Delta S^{\ddagger} = 13.8$ eu, $\Delta G^{\ddagger}$ ($-105°$) = 8.2 kcal/mol. The spectra are not reproduced here because they are of the standard A_2-to-AB form. A complete line-shape analysis was not feasible with the tellurane because lines were extremely broad.

The rather unusual changes in the spectrum of the α protons of selenane-*3,3,5,5-d*$_4$ 1-oxide (**4**) are illustrated in Figure 1. At room temperature a singlet is observed with small wings. As the temperature is lowered, the resonance passes through a series of very unsymmetrical line shapes, but finally a nearly symmetrical AB quartet is observed at $-130°$. A small doublet appears to lower field of the AB quartet. With the peaks numbered 1-6 from lowest to highest field, peaks 3-6 correspond to the axial and equatorial resonances of the dominant isomer in eq 1. Peaks 1 and 2 and a mirror-image doublet under peaks 5 and 6 form an AB quartet from the minor isomer. Location of the small up-field doublet was derived not only from clear perturbations in spectral intensities but also from the requirements to fit the fast-exchange spectrum. Any other placement failed to give the required singlet structure. A complete line-shape fit of these spectral changes was achieved with a program[12c] that allows two slow-exchange AB spectra to pass to a single fast-exchange AB spectrum. Crossover averaging is observed,[12c,16] since the low-field (equatorial) protons of the minor isomer exchange with the high-field (axial) protons of the major isomer, and the high-field (axial) protons of the minor isomer exchange with the low-field (equatorial) protons of the major isomer. Arguments presented in the next section show that the minor isomer has the oxide group equatorial and the major isomer the oxide group axial. Direct integration of the spectrum and the requirements of the line-shape fit indicate that there is 84% of the axial isomer and 16% of the equatorial isomer. The γ-proton resonance remains a single AB quartet over the entire temperature range.

The spectral parameters for selenane oxide are presented in Table II, together with parallel data[12c] for the corresponding sulfur compound, thiane oxide. The latter data will be needed in the ensuing discussion. Activation parameters for ring reversal were calculated from the mean lifetimes (see caption to Figure 1) derived from the complete line-shape analysis. Because of the substantial free-energy difference between the axial and equatorial isomers (475 cal/mol), the activation parameters are strongly dependent on the direction of the reaction. For the axial-to-equatorial direction, the following parameters were obtained: $E_a = 8.2$ kcal/mol, $\log A = 12.2$, $\Delta H^{\ddagger} = 7.6$ kcal/mol, $\Delta S^{\ddagger} = -4.7$ eu, $\Delta G^{\ddagger}$ ($-102°$) = 8.4 kcal/mol, correlation coefficient 0.995; for the equatorial-to-axial direction $E_a = 8.2$ kcal/mol, $\log A = 12.9$, $\Delta H^{\ddagger} = 7.6$ kcal/mol, $\Delta S^{\ddagger} = -1.5$ eu, $\Delta G^{\ddagger}$ ($-102°$) = 7.9 kcal/mol, correlation coefficient 0.995.

Table II. Spectral Parameters for Selenane Oxide and Thiane Oxide

	S[a]	Se
Solvent	CH_2Cl_2	$CHClF_2$
$\delta_{ae}(\alpha)$[b]	0.87	0.80
$J_{ae}(\alpha)$	11.7	10.0
Pop.	0.38	0.16
$\delta_{ae}'(\alpha)$	0.48	0.25
$J_{ae}'(\alpha)$	13.7	12.9
Pop.′	0.62	0.84
Temp, °C	−90	−130
$\Delta G°$, cal/mol[c]	−175	−475

[a] Data from ref 12c. [b] Chemical shift differences are in ppm (±0.01) and coupling constants in Hz (±0.1); δ, J, and Pop. refer to the lower-field (equatorial oxide) isomer; δ', J', and Pop.′ to the higher field (axial oxide) isomer. [c] The negative sign denotes a preference for the axial isomer.

The fast exchange spectra of the α and γ protons of selenane-*3,3,5,5-d*$_4$ 1,1-dioxide (**5**) are the usual singlets in 1:10 $CH_2Cl_2/CHClF_2$. No change is observed in the α-proton resonance down to $-150°$, just as with the sulfur analog.[10] The γ-proton resonance, however, passes through a coalescence temperature of $-133°$ to give an AB spectrum at $-141°$, $\delta_{ae}(\gamma)$ 0.39 ppm, $J_{ae}(\gamma) = 14.0$ Hz. A complete line-shape analysis was not carried out, but the free energy of activation at the coalescence temperature was determined to be 6.7 kcal/mol. A line-shape fit at this one temperature gave an identical value.

Except for small changes in chemical shifts, the spectrum of the methylselenonium salt (**6**) is invariant with temperatures between +27 and $-88°$ in SO_2/CH_2Cl_2. Lower temperatures were not possible in this solvent system or in SO_2FCl, freons, vinyl chloride, and mixtures of these with SO_2. The α-proton resonance at 27° is an AB quartet with $\delta_{ae}(\alpha)$ 0.31 ppm and $J_{ae}(\alpha) = 12.4$ Hz; at $-88°$ $\delta_{ae}(\alpha)$ 0.24 ppm and $J_{ae}(\alpha) = 12.4$ Hz. The γ-proton resonance at 27° is a tightly coupled AB, whereas at $-88°$ the separation is much larger: $\delta_{ae}(\gamma)$ 0.189 ppm and $J_{ae}(\gamma) = 14.0$ Hz. These spectra are probably taken above a coalescence temperature, in light of the values obtained for the other selenane derivatives. The equilibrium, however, is clearly biased to one conformational form, since the coupling constant is invariant with temperature and the fast-exchange α-resonance has a large chemical-shift difference. Crossover averaging brings about very small fast-exchange chemical shift differences, as in Figure 1.[16] The change in the magnitude of δ_{ae} therefore comes not from a shift in an equilibrium between two species but from changes in the chemical shifts themselves. Such changes have been observed frequently in other similar systems.[17]

For comparison, we have also examined the methylsulfonium analog of **6**, *S*-methylthianium iodide, in SO_2/CH_2Cl_2. At room temperature, the α-proton resonance consists of an AB quartet, $\delta_{ae}(\alpha)$ 0.31 ppm and $J_{ae}(\alpha) = 12.3$ Hz. At $-88°$, only small changes in chemical shifts are observed, $\delta_{ae}(\alpha)$ 0.23 ppm and $J_{ae}(\alpha) = 12.3$ Hz. The γ protons gave a tightly coupled AB spectrum and the methyl protons a sharp singlet throughout the temperature range. The constancy of the α-coupling constant again suggests that only one member of the equilibrium of eq 1 is present.

The coalescence temperatures and free energies of activation measured in this study are collected in Table III.

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(16) J. B. Lambert, C. E. Mixan, and D. S. Bailey, *J. Amer. Chem. Soc.*, **94**, 208 (1972).

(17) J. B. Lambert, D. S. Bailey, and C. E. Mixan, *J. Org. Chem.*, 37, 377 (1972).

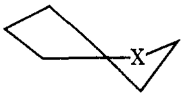
Table III. Free Energies of Activation to Ring Reversal in Group VI Pentamethylene Heterocycles

Hetero group	T_c, °C	$\Delta G^{\ddagger}$ (T_c), kcal/mol
O	−61	10.3
S	−81	9.4
Se	−105	8.2
Te	−119	7.3
S=O[a]	−70[b]	10.1[c]
Se=O	−102	8.3[c]
SO_2[d]	−63[b]	10.3
SeO_2	−133	6.7

[a] Data from ref 12c. [b] Measured at 60 MHz; others measured at 90 MHz. [c] Weighted-average value of both conformers, measured by the complete line-shape method; others measured by the coalescence-temperature method. [d] Data from ref 10.

Discussion

The primary source of the increase in energy on going from the ground-state chair to the transition-state half-chair in the process of ring reversal is the increase in torsional strain. Contributions from nonbonded interactions and particularly angle-bending strain are thought to be much smaller.[18] Allinger, for example, calculates that bending strain contributes only 2 out of 12 kcal/mol to the cyclohexane barrier.[18b] There are three possible half-chair transition states for a six-membered ring containing only one heteroatom, **7–9**. An estimate of torsional interactions can be obtained from the barriers to CH_3–X rotation in molecules of the type CH_3–X–CH_3 (Table IV). Thus, in molecules for which the C–X torsional barrier is lower than that of the C—C bond, the preferred transition state will be **7**, in which the heteroatom relieves the greatest amount of eclipsing strain. On the other hand, in molecules for which C–X torsion is of higher energy than C–C torsion, transition state **9** is to be preferred, since the heteroatom is located in the least eclipsed portion of the molecule. Nearly equivalent torsional barriers might result in any of these transition states (**7–9**).



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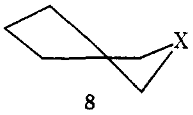

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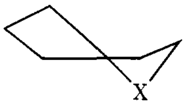

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Table IV. Torsional Barriers in Molecules of the Type CH_3-X-CH_2

X	V_0, kcal/mol	Source
CH_2	3.3	*a*
NH	3.28	*b*
NCH_3	4.40	*c*
O	2.50	*d*
S	2.13	*e*
Se	1.50	*f*
Te	(1.2)	*g*
S=O	2.94	*h*
C=O	0.78	*i*
SiH_2	1.65	*j*

[a] G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **8**, 610 (1940); K. S. Pitzer and W. D. Gwinn, *ibid.*, **10**, 428 (1942). [b] W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, **18**, 977 (1962). [c] D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **28**, 572 (1958). [d] J. R. Durig and Y. S. Li, *J. Mol. Struct.*, **13**, 459 (1972). [e] L. Pierce and M. Hayashi, *J. Chem. Phys.*, **35**, 479 (1961). [f] J. F. Beecher, *J. Mol. Spectrosc.*, **21**, 414 (1966). [g] Estimated from data in the solid: J. R. Durig, C. M. Player, Jr., J. Bragin, and Y. S. Li, *J. Chem. Phys.*, **55**, 2895 (1971). [h] H. Dreizler and G. Dendl, *Z. Naturforsch. A*, **20**, 1431 (1965). [i] J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, **31**, 1562 (1959). [j] L. Pierce, *ibid.*, **34**, 498 (1961).

The simplest approach to the analysis of ring reversal, substantiated by more refined calculations,[18a] therefore is to relate the height of the barrier to the C–X torsional energy (Table IV). The lower ring reversal barriers (with respect to cyclohexane) in piperidine (NH), thiane (S), and tetrahydropyran (O), and the higher barrier in *N*-methylpiperidine (NCH_3) have been rationalized in terms of analogous changes in the C–X torsional barrier.[18a] All the barriers reported in the present study for selenanes and telluranes (Table III) are lower than that of cyclohexane. The most likely half-chair transition state therefore is **7**. For each oxidation state, the ring-reversal barrier is lower for the selenium molecule than for the corresponding sulfur molecule, and our one example of a tellurium heterocycle has a lower barrier still. In the parent heterocycle series (O, S, Se, Te), there is a drop of about 1 kcal/mol with each row in the periodic table. The difference between the sulfoxide and the selenoxide is about 2 kcal/mol, and the difference between the sulfone and the selenone is more than 3 kcal/mol. It is noted that the sulfone barrier is slightly larger than the sulfoxide barrier, which is clearly larger than the sulfide barrier ($SO_2 \sim SO > S$). To the extent that the data are available, these results parallel the C–X torsional barriers (Table IV). The monotonic drop in the barrier to ring reversal from thiane to tellurane is caused by the parallel drop in the C–X torsional energy.[19] In the sulfur series, the increase in the barrier for the sulfoxide over that for the sulfide is caused by the increased C–SO torsional energy (compare dimethyl sulfoxide with dimethyl sulfide). From the slightly larger ring-reversal barrier for the cyclic sulfone, the torsional energy in dimethyl sulfone can be expected to be as large or larger than that in dimethyl sulfoxide. The barriers to ring reversal in the selenium series present a contrasting order. The selenide and selenoxide barriers are essentially the same, and both are clearly larger than the selenone barrier ($Se \sim SeO > SeO_2$). Although the data are not available for dimethyl selenoxide and dimethyl selenone, on this basis we would predict that the torsional barriers follow the order $CH_3\text{–}Se \sim CH_3\text{–}(SeO) > CH_3\text{–}(SeO_2)$.

The overall shape of the ring has little to do with the magnitude of the barrier to ring reversal. The flattened ring of cyclohexanone (*R* value 1.72)[9] has a barrier that is much smaller than that of cyclohexane, but the barriers in the group VI series decrease with increased ring puckering: tetrahydropyran (*R* 1.91), thiane (2.61), selenane (2.74), tellurane (2.76). If angle-bending strain were a dominant factor, ring shape would have been important. Cyclohexanone, with one sp^2 carbon, can assume the half-chair transition state with a smaller amount of angle strain than cyclohexane. For the group VI heterocycles, the C–X–C angle is much

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(18) (a) R. K. Harris and R. A. Spragg, *J. Chem. Soc. B*, 684 (1968); (b) N. L. Allinger, M. A. Miller, F. A. VanCatledge, and J. A. Hirsch, *J. Amer. Chem. Soc.*, **89**, 4345 (1967).

(19) For a review of torsional energies, see J. Dale, *Tetrahedron*, 22, 3373 (1966).

smaller than that in cyclohexane, so placement of the heteroatom in the position illustrated in **7** would increase angle strain. The observed monotonic decrease in the barrier going down group VI indicates that torsional effects must far outweigh angle-bending strain.

The remainder of the discussion will be concerned with the position of the equilibrium of eq 1 for the oxides and the methyl onium salts. Configurational criteria have been established for the thiane series to determine the location of the substituent at the 1 position. Invariably, for molecules carrying a single substituent on the heteroatom and none elsewhere, the axial isomer (equatorial lone pair) has the smaller α-proton chemical shift difference ($\delta_{ae}(\alpha)$), the larger coupling constant ($J_{ae}(\alpha)$), and the higher field AB-quartet midpoint..[12c,16,17,20] The coupling constant criterion appears to remain valid even in the presence of other ring substituents, but the chemical shift criterion has some exceptions.[16,17] The molecules in the present study bear only substituents at the 1 position, so all three criteria should be applicable, although conclusions are difficult when only one conformer is observed. Table V summarizes pertinent α-proton geminal coupling constants measured previously and in this study. It can be seen that the value of $J_{ae}(\alpha)$ invariably is close to 14 Hz when the substituent on sulfur is axial (lone pair equatorial and close to 12 Hz when it is equatorial (lone pair axial).

Table V. Geminal Coupling Constants (Hz) at the α Position in 1-Substituted Pentamethylene Heterocycles

X–Y[a]	*J* (Y-axial)	*J* (Y-equatorial)	Ref
$^+S\text{–}H$	15.0		10
$^+S\text{–}H$[b]	15.0		17
$^+S\text{–}H$[c]	14.5		17
S=O	13.7	11.7	12c
S=O[b]	14.9	12.4	17
S=NH	13.8	12.0	16
S=NTs[d]	14.4	12.0	16
S=NTs[b]	14.8	12.5	17
S=NBzs[d]	14.7	12.4	16
$^+S\text{—}CH_3$		12.3	This work
$^+Se\text{—}H$	13.0		10
Se=O	12.9	10.0	This work
$^+Se\text{—}CH_3$	12.4		This work

[a] See eq 1. [b] 4,4-Dimethyl derivative. [c] 3,3-Dimethyl derivative. [d] Ts represents *p*-toluenesulfonyl and Bzs represents benzenesulfonyl.

We will first examine the results for the selenoxide (**4**). The major isomer has a $\delta_{ae}(\alpha)$ of 0.25 ppm and a $J_{ae}(\alpha)$ of 12.9 Hz (Table II), and the spectral midpoint (Figure 1) is clearly at higher field. The minor isomer has a $\delta_{ae}(\alpha)$ of 0.80 and a $J_{ae}(\alpha)$ of 10.0, and the spectral midpoint is at lower field. All three criteria established for sulfur systems[12c,16,17,20] (Table V) are in agreement that the major isomer has the oxide axial (lone pair equatorial). It is noted that the values of $J_{ae}(\alpha)$ for the selenium series are consistently about 1.5 Hz smaller than those for the sulfur series, as in the parent compounds (Table I), selenane (12.3 Hz) and thiane (13.6), because of differences in electronegativity and other factors. The coupling constants for thiane 1-oxide are 13.7 and 11.7 Hz, whereas those for selenane 1-oxide are 12.9 and 10.0 Hz. The coupling constant for the axial oxide isomer and that previously measured[10] for protonated selenane (axial proton) are essentially identical. The geminal coupling constants between γ protons are insensitive to all these effects: thiane (13.9 Hz), selenane (13.9), axial thiane 1-oxide (14.3), equatorial thiane 1-oxide (14.0), sulfone (14.0), selenone (14.0), *Se*-methylselenanium iodide (14.0).

The selenoxide has a larger proportion (84% at $-130°$) of axial conformer than does the sulfoxide (62% at $-90°$, or 65% extrapolated to $-130°$ assuming a constant $\Delta G°$). The longer carbon-selenium bond therefore renders the 1.3 and 1.5 interactions more attractive than in the sulfur case. We do not know if the selenoxide offers the optimal distance between the 1-oxide and the 3.5 protons and carbons. In order to decide whether the best distance has been reached or exceeded, data from systems such as tellurane 1-oxide with even longer bonds would be required.

In contrast to thiane 1-oxide[12] and protonated thiane,[10] the methylsulfonium salt has not been the subject of an independent configurational assignment. The coupling constant (12.3 Hz), however, is clearly in the range for an equatorial isomer (Table V). Evidence was given in the previous section that only one isomer is present. The constancy of $J_{ae}(\alpha)$ with temperature and the large fast-exchange value of $\delta_{ae}(\alpha)$ could nonetheless be consistent with as much as 10% of a second isomer. The fast-exchange spectrum of selenane 1-oxide (Figure 1) shows how crossover averaging causes the AB quartet to be very closely coupled (small $\delta_{ae}(\alpha)$) when the minor isomer amounts to only 16%. On the basis of the magnitude and constancy of $J_{ae}(\alpha)$, we conclude that *S*-methylthianium iodide is at least 90% equatorial. Chemical shift comparisons were not used in this context because of their greater sensitivity to extraneous factors.[16,17] Although comparison of $\delta_{ae}(\alpha)$ for a pair of epimers can be useful, transfer between nonepimeric systems must be done with extreme care. We have found that $J_{ae}(\alpha)$ on the other hand is a much more general criterion.[16,17] Had both $^+S\text{-}CH_3$ conformers been available, we would have applied the $\delta_{ae}(\alpha)$ criterion, but with only one isomer, we utilize the $J_{ae}(\alpha)$ criterion alone.

The methylselenonium salt presents a contrasting situation. The value of $J_{ae}(\alpha)$ (12.4 Hz) is very close to those of the axial-protonated selenane and the axial selenoxide, and about 2.5 Hz larger than that of the equatorial selenoxide (Table V). The conclusion to be drawn is that the 1-methyl group must be predominantly axial. Once again the value of $J_{ae}(\alpha)$ is constant over the entire temperature range, and the fast-exchange value of $\delta_{ae}(\alpha)$ is large. The lowest temperature ($-88°$) is probably higher than a possible coalescence temperature, so an admixture of a small amount (<10%) of the equatorial isomer cannot be rejected.

It may prove that the axial preference for substituents is the rule rather than the exception in six-membered rings containing heteroatoms from below the second row. As the conformational analysis of phosphacyclohexanes[6] and silacyclohexanes[5] is unraveled, more and more examples of axial preferences are being revealed.

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(20) Y. Allingham, R. C. Cookson, and T. A. Crabb, *Tetrahedron* **24**, 1989 (1968); R. Cahill, R. C. Cookson, and T. A. Crabb, *ibid.*, **25**, 4681 (1969).

The evidence we present in this paper indicates that this pattern will be followed in group VI heterocycles.

Summary

The barrier-to-ring reversal decreases monotonically on going down the column for group VI pentamethylene heterocycles, despite the fact the ring is becoinmg increasingly puckered. The lower barrier is associated with the smaller C–X torsional barrier, and angle-bending strain must be unimportant. The same pattern is observed for the oxides and dioxides of thiane and selenane (SO > SeO; $SO_2 > SeO_2$). For the selenium series, the prediction can be made that the order of torsional barriers should be dimethyl selenide ∼ dimethyl selenoxide > dimethyl selenone, whereas in the sulfur series the predicted order is dimethyl sulfone ∼ dimethyl sulfoxide (known) > dimethyl sulfide (known). Selenane 1-oxide is found to have a larger proportion of axial isomer (84%) than thiane 1-oxide (62%) because the longer carbon-selenium bond length produces more attractive 1,3 and 1,5 interactions. For the same reason, *Se*-methylselenanium iodide appears to be almost entirely axial, whereas *S*-methylthianium iodide is almost entirely equatorial, on the basis of the magnitude of the α-proton geminal coupling constant.

Experimental Section

Melting points were measured with a Hershberg apparatus and are uncorrected. Routine nmr spectra were recorded on Varian A-60 and T-60 spectrometers. Variable-temperature experiments were conducted on the 90-MHz Bruker HFX-10 spectrometer, equipped with a Nicolet 1074 signal-averaging computer. Temperatures were calibrated with a Wilmad low-temperature thermometer and are considered accurate to ±1°. Complete line-shape analyses were carried out on a CDC-6400 computer with a CalComp 565 plotter. Elemental analyses were performed by Miss H. Beck, Analytical Services Laboratory, Department of Chemistry, Northwestern University, and by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Selenane-*3,3,5,5*-d_4 (2). The method is an adaptation of that of McCullough and Lefohn[21] and has been described previously.[11a]

Selenane-*3,3,5,5*-d_4 1-Oxide (4). A mixture of 0.75 g (0.005 mol) of deuterated selenane and 0.60 g (0.005 mol) of 30% H_2O_2 was shaken in a sealed tube until only one layer was present. After standing overnight, the solution was extracted three times with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$. Removal of the drying agent and the solvent produced the crystalline but hygroscopic selenoxide. Recrystallization from benzene under anhydrous conditions gave 0.20 g of white crystals: mp 129–130.5° (sealed tube); nmr (CH_2Cl_2) δ 2.60 (br s, 4, α CH_2) and 1.50 (AB q, 2, J = 13.6 Hz, γ CH_2). *Anal.* Calcd for $C_5H_{10}OSe$: C, 36.36; H, 6.06. Found: C, 36.23; H, 6.10.

Selenane-*3,3,5,5*-d_4 1,1-dioxide (5) was obtained by the same method as the selenoxide, with 2 equiv of H_2O_2 and some heating on a steam bath: mp 190–191°; nmr (CH_2Cl_2) δ 3.18 (s, 4, α CH_2) and 1.60 (s, 2, γ CH_2). *Anal.* Calcd for $C_5H_{10}O_2Se$: C, 33.15; H, 5.52. Found: C, 32.81; H, 5.63.

***Se*-Methylselenanium-*3,3,5,5*-d_4 iodide (*Se*-methylpentamethyleneselenonium iodide) (6)** was prepared by stirring the deuterated selenane (**2**) with an excess of CH_3I until a white precipitate had formed. The solid was filtered, washed with CH_2Cl_2, and dried to give a quantitative yield of the salt: mp 176–178° (sealed tube, sublimed); nmr (SO_2/CH_2Cl_2) δ 3.24 (AB q, 4, J = 12.4 Hz, α CH_2), 2.66 (s, 3, CH_3), and 1.65 (s, 2, γ CH_2). *Anal.* Calcd for $C_6H_{13}SeI$: C, 24.74; H, 4.47. Found: C, 24.43; H, 4.46.

***S*-Methylthianium-*3,3,5,5*-d_4 iodide (*S*-methylpentamethylenesulfonium iodide)** was prepared from thiane[12c] in the same manner as the selenium analog:[22] mp 196–197° (sealed tube, sublimed); nmr (SO_2/CH_2Cl_2) δ 3.24 (AB q, 4, J = 12.3 Hz, α CH_2), 2.66 (s, 2, γ CH_2), 1.98 (s, 3, CH_3). *Anal.* Calcd for $C_6H_{13}SI$: C, 29.51; H, 5.33. Found: C, 29.68; H, 5.48.

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[21] J. D. McCullough and A. Lefohn, *Inorg. Chem.*, **5**, 150 (1966).

[22] This material was first prepared by R. G. Keske, to whom we are grateful for the instructions.

Conformational and Stereochemical Consequences of Uniparticulate Electrophilic Additions to *cis*-Bicyclo[6.1.0]nonatrienes. Reactions with Tetracyanoethylene

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Abstract: Reaction of *cis*-bicyclo[6.1.0]nona-2,4,6-triene and its *anti*-9-methyl and *anti*-9-chloro derivatives with TCNE produces bicyclic tetracyanocyclobutanes in which the four-membered moiety is trans fused to a cyclononatriene ring. The methyl and chlorine substituents have been found to occupy uniquely the 6 position and to be oriented stereochemically trans to H_1 and cis to H_9. These studies reveal that TCNE is functioning as a uniparticulate electrophile and suggest that intermediate dipolar species possessing the gross structural features of *trans*-1,3-bishomotropylium ions are transiently produced. In addition, the lack of reactivity of bicyclo[6.1.0]-nonatrienes endowed with syn-9 substituents attests to the involvement of the more strained folded conformation of the bicyclic triene. The causative factors underlying the greater reactivity of the less stable conformers and the kinetic preference of the electrophile for exo bonding at C_3 are discussed.

A number of mechanistically informative and synthetically useful applications of uniparticulate electrophilic addition have recently been reported and discussed.[4,5] The unusually effective capability of such reagents to intercept transient cationic interme-

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