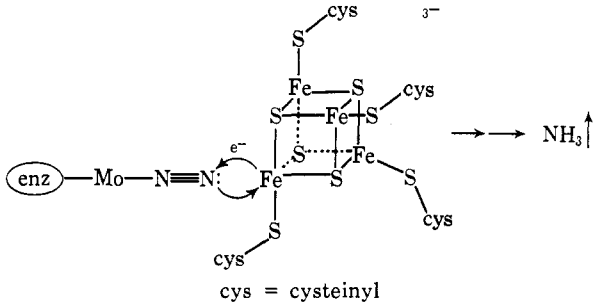
12 hr more, the reaction mixture was worked up, and $^{15}NH_3$ yields were determined mass spectrometrically (up to 0.012 mol/mol of **1**).[6c] In additional experiments involving 2^{3-} and **1**, yields of $^{15}NH_3$ produced through use of NaAc fell at much lower levels, and the stronger reducing agents NaAn and NaPy were even less effective. No $^{15}NH_3$ was generated by the action of NaAc, NaFl, NaAn, NaPy, 2^{2-}, 2^{3-}, or 2^{4-} alone on $^{15}N_2$ labeled **1**, but NaNp was effective, even in only a sixfold excess. When unlabeled, $^{14}N_2$ **1** was employed in various fixation experiments, larger (0.02–0.04 mol/mol of **1**) NH_3 yields were sometimes generated, presumably a consequence of an impurity present in the preparation of **1** utilized.[9,10]

In order to compare more fully with the biological N_2-fixation system, the action of 2^{n-} on nitrogenase substrates other than N_2 was studied. Whereas the enzyme converts alkyl cyanide to hydrocarbon,[11] 2^{2-}, 2^{3-}, and 2^{4-} were without action on this organic species. However, as in the biological system, 2^{3-} and 2^{4-} converted isocyanide ($C_{12}H_{25}NC$) to amine ($C_{12}H_{25}NH_2$) and 2^{4-} reduced alkyne (decyne-1) to alkene (decene-1, accompanied by some decyne-2). Interestingly, Δ^2-nonenylnitrile was also transformed by 2^{4-} in smaller yield to decene-1.

The body of results herein clearly points to the unique role of 2^{3-} in the abiological fixation of Mo-bound N_2. Assuming direct interaction of **1** and **2**, we believe it likely that the Mo-bound N_2 unit interacts at a corner of the cluster cube (as depicted), especially because of the available Fe coordination sites.[12] Whether the lone electron pair or the π-electrons (or both) of the N_2 ligand are involved in this binding cannot be said at this time. The subsequent radical anion reduction of Mo–Fe bound N_2 may be coordinated with electron transfer from 2^{3-}, possibly facilitated by involvement of the sulfide and/or mercaptide ligands. The biological relevance of these laboratory reactions is underscored by the electronic and structural identity of 4Fe–4S cubic cores in the reduced bacterial ferredoxins and these synthetic 2^{3-} systems.[2] Assuming that nature can avail itself of a chemical pathway of the type described herein, we propose that the enzymic N_2 fixation reaction proceeds as shown below.



cys = cysteinyl

(9) In the molybdenum series, the reported formation of $^{14}NH_3$ resulting from the action of 2 equiv of **3** pretreated with 8–16 equiv of NaNp[8] may be due to the presence of a non-nitride contaminant (reducible to the NH_3 level but not subject to $^{15}N_2$ exchange) generated during the preparation of **1**.[1]

(10) Lecture, 24th Congress of the International Union of Pure and Applied Chemistry, Hamburg, Sept 4, 1973.

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(13) National Science Foundation Fellow, 1971–1974.
(14) Deutsche Forschungsgemeinschaft Fellow, 1973.

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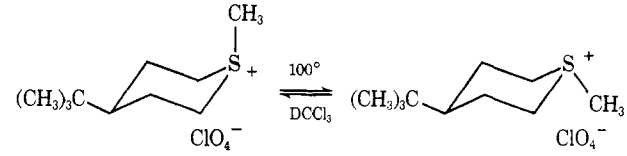
Conformational Equilibrium in *S*-Methylthianium Perchlorate

Sir:

The energy difference between equatorial and axial methyl in methyl-substituted cyclohexanes was determined very early in the development of conformational analysis and with high accuracy;[1,2] the equatorial conformation is preferred by 1.7 ± 0.1 kcal/mol in the liquid phase. For some time thereafter it was believed that equatorial substituents were, quite generally, more stable than axial ones; one of the earliest findings to dispel this notion was the discovery[3] that the preferred conformation in thiacyclohexane sulfoxide is the one with axial oxygen ($\Delta G°$ = 0.2–1.3 kcal/mol).[3] In recent years, quite a number of cases of preferential stability of axial conformations have come to light;[4] most of these involve heteroatoms as one of the interacting partners. One that does not and yet lacks equatorial preference of the methyl group is *P*-methylphosphacyclohexane in which $\Delta G°$ for the *P*-methyl group is near zero.[5] In contrast, it has been reported[6] that in thiacyclohexylmethylsulfonium salts the *S*-methyl group is largely equatorial; this claim is, however, based on possibly unsafe considerations of geminal coupling constants of the protons at C(2) and C(6).

Since, in connection with another problem,[7] we were vitally interested in the *S*-methylthianium equilibrium, we decided to synthesize the model 4-*tert*-butyl compounds (**1** and **2**) shown in Scheme I and to study their equilibration. The salts were easy to prepare in a *ca.*

Scheme I



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(7) O. Hofer and E. L. Eliel, *J. Amer. Chem. Soc.*, **95**, 8045 (1973).

12:88 ratio by derivatization of the parent thiane[3] with methyl iodide followed by anion exchange with a Dowex 1X8-100 resin (hydroxide form) followed by neutralization with perchloric acid and were separated by crystallization from water: predominating isomer, mp 149–150°, minor isomer, mp 173–174°.[8] Configuration was assigned on the basis of cmr spectra; isomer **2** of mp 149–150°, formed in major amount has the downfield *S*-methyl (25.48 ppm from TMS) and 3,5-methylene (25.10 ppm) groups whereas the more compressed axial isomer **1** displayed the upfield methyl (16.61 ppm) and 3,5-methylene (19.04 ppm) signals, as might be expected on the basis of analogy with methylcyclohexanes.[9] The configurations were proved beyond the shadow of a doubt by X-ray crystallographic analysis of both isomers.

Crystals of **1** are orthorhombic, space group $P2_12_12_1$ (D_2^4), $a = 11.02 \pm 0.01$, $b = 13.57 \pm 0.01$, $c = 9.25 \pm 0.01$ Å, $Z = 4$. Isomer **2** crystallizes in the orthorhombic system, space group $Pbca$ (D_{2h}^{15}), $a = 13.25 \pm 0.01$, $b = 12.59 \pm 0.01$, $c = 17.22 \pm 0.01$ Å, $Z = 8$. Intensity data were recorded on an Enraf-Nonius CAD-3 diffractometer operating in the θ–2θ scanning mode with Zr-filtered Mo Kα (λ 0.7107 Å) radiation. Both structures were solved by the heavy-atom approach and the atomic parameters (anisotropic C, Cl, O, S; fixed H contributions) were refined by full-matrix least-squares calculations to $R = 0.063$ over 875 observed reflections [$I > 2\sigma(I)$] for **1** and $R = 0.104$ over 890 reflections for **2**.

In addition to verifying isomer assignments the X-ray investigations provide details of the molecular dimensions which reveal no significant differences between the isomers *except* around C(2),C(6) where the mean value (assuming C_s molecular symmetry) of the C–C–S angle is 106.8 ± 1.0° for **2** and 115.3 ± 0.6° for **1**. Associated mean endocyclic dihedral angles C(6)SC(2)C(3) and SC(2)C(3)C(4) are 64 and 69°, respectively, for **2** in contrast to substantially smaller values of 46 and 59° in **1**, the differences being a measure of the ring flattening which occurs at sulfur in the axial methyl isomer **1** in order to relieve overcrowding with the syn-axial hydrogens.

Equilibration of the two isomers at 100° in chloroform-*d* for 57 hr led to identical equilibrium mixtures as shown by pmr; the ratio of the area of the methyl signal of **2** (3.03 ppm) to that of **1** (2.93 ppm) was 1.42. The composition was confirmed by a quantitative ^{13}C analysis of the mixture on a Varian XL-100 instrument with Fourier transform using gated decoupling and a 60-sec pulse delay time to minimize effects of nuclear Overhauser enhancement and of possibly unequal relaxation times of corresponding carbon nuclei; the ratio of the *S*-methyl signals of the two isomers was 1.48 and that of the 3,5-methylene signals 1.45. We thus conclude that $K = 1.45 \pm 0.05$ at 100° and $\Delta G°_{100} = -0.275$ kcal/mol favoring the equatorial isomer. The equilibrium position of the unbiased *S*-methylthianium perchlorate (**3**) is probably very similar, since the 4-*tert*-butyl group does not usually cause a major disturbance in the direct equilibration method.[10] Accordingly, the *S*-methyl ^{13}C resonance of **3** was found at 22.10 ppm (calcd δ 22.06 ppm from $\delta = \delta_a/(K + 1) + K\delta_e/(K + 1)$ and $K^{25}_{\text{calcd}} = 1.592$ assuming $\Delta G_{25}° = \Delta G_{100}°$).

In the case of sulfoxides, it has been calculated[11] that the axial isomer is preferred because of a dominating O/H attraction. In the *S*-methylthianium salts, there is a slight net axial repulsion, but much smaller in magnitude than that in axial methylcyclohexane. If one constructs a model of the axial isomer **1** with the equatorial ring geometry (which might be considered the "natural" geometry of the thianium ring) one finds that the $CH_3/H(3,5)$ distance d is nearly the same in the sulfur compound as in axial methylcyclohexane, as a result of a compensation of the increased ring-CH_3 bond length (which increases d) and the increased ring puckering (which decreases d). The large change of torsion angles in **1** (as compared to **2**) indicates, however, that there is a very facile (*i.e.*, energetically cheap) flattening of the ring which greatly increases d and thus diminishes the energy of the axial form **1**. An energetically cheap deformation of comparable magnitude is not possible in axial methylcyclohexane, presumably due to steric problems caused by the geminal equatorial hydrogen on the ring atom bearing the methyl group.[12] In the sulfonium salt **1** this hydrogen atom is replaced by an unshared electron pair, which evidently offers much less resistance to strain relief of the axial methyl group by torsional deformation.

Supplemental Material Available. A listing of atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-3021.

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Lanthanide Shift Reagents. A Model Which Accounts for the Apparent Axial Symmetry of Shift Reagent Adducts in Solution

Sir:

Insofar as nuclear resonance displacements induced by lanthanide shift reagents (LSR's) are dipolar in origin, they hold the promise of supplying valuable information about the geometries and conformations of substrate molecules in solution.[1] Equation 1 gives the

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