

respectively; we have assumed that the back-reaction is unimportant, and  $[NE] > [V(NE)_2]$ .

The longest transient can be ascribed to further reactions of the quinone products of the redox reaction. These reactions include semiquinone quenching, oxidative addition of hydroxide to the quinone, and other processes.<sup>8</sup>

Reversal of the vanadate inhibition of (Na,K)-ATPase is accomplished by norepinephrine and other catecholamines through complexation and reduction of vanadate. These compounds are more effective in removing free vanadate than other chelators (e.g., EDTA) under physiological conditions because they do not readily form competing complexes with  $Mg^{2+}$  and  $Ca^{2+}$ .<sup>9</sup> Thus, the model presented here is consistent with the data, and explains several other related observations.

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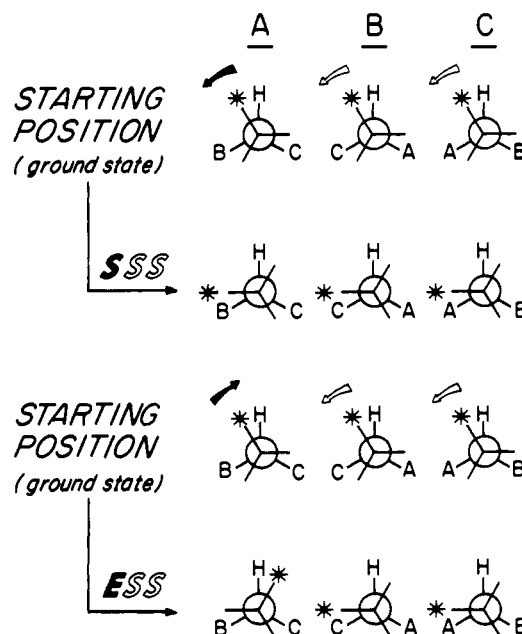
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### Correlated Rotation of *tert*-Butyl Groups in Tri-*tert*-butylsilane

Sir:

In crowded systems, the correlated (coupled) rotation of two or more alkyl groups may become energetically more feasible than the independent rotation of a single group.<sup>1</sup> In view of current interest in "gearing" or "cogging" effects of alkyl groups,<sup>2-5</sup> we now wish to report evidence based on empirical force field (EFF) calculations<sup>6</sup> and DNMR studies that the rotation of the *tert*-butyl groups in tri-*tert*-butylsilane (**1**) is correlated.

According to full relaxation EFF calculations, the ground state of **1** has  $C_3$  symmetry, with torsional angles ( $\phi = C_m-C_q-Si-H$ )<sup>8</sup> of 43°. To study dynamic processes in **1**, we resorted to incremental group driving calculations.<sup>14</sup> Using this



**Figure 1.** Two torsional pathways for *t*-Bu<sub>3</sub>SiH (see text). The view down the C<sub>q</sub>-Si bond axis from C<sub>q</sub> to Si is shown for each of the three *tert*-butyl groups (A, B, and C, as denoted by the column heading). One methyl in each *tert*-butyl group is marked with a star to provide a point of reference. Solid arrows indicate the direction in which group A is driven; hollow arrows indicate the overall direction of rotation induced in the other two groups.

method, strain energies of **1** were calculated<sup>6</sup> with one C<sub>m</sub>-C<sub>q</sub>-Si-H torsional angle frozen at successively increasing or decreasing values,<sup>15</sup> while all other internal parameters were allowed full relaxation. When one *tert*-butyl group of **1** was driven through a staggered (*S*) conformation, a barrier of 5.1 kcal/mol was surmounted as the other two (unfrozen) *tert*-butyl groups responded by rotating through staggered conformations, resulting in overall enantiomerization by the SSS pathway (Figure 1). When the *tert*-butyl group was driven through the eclipsed (*E*) conformation, the other two groups again responded by rotating through staggered conformations (ESS, Figure 1), with a calculated barrier of 6.8 kcal/mol. These two processes represent correlated rotations, in the following sense.

The possible torsional pathways which effect topomerization or enantiomerization can be delineated by means of group theoretic techniques.<sup>16</sup> Considering only rotations about the *t*-Bu-Si bonds,<sup>17</sup> the C<sub>3</sub> point group partitions the nonrigid molecular symmetry group of feasible rearrangements<sup>18</sup> ( $G_{162} = (C_3)^3 \wedge C_{3v}$ ) into sixteen distinct rearrangement modes: ten enantiomerizations (two of which are represented by the SSS and ESS processes), five topomerizations, and the identity mode. We consider rotation to be correlated if, and only if, a single-step process leads to permutational rearrangement (site exchange) of the methyl groups in more than one of the three *tert*-butyl groups. It follows that all enantiomerizations, including the two processes depicted in Figure 1, involve correlated rotations.

In the threshold (SSS) mechanism, all three *tert*-butyl groups undergo net conrotation (see Figure 1). Two of the three diastereotopic methyl sites are thus rendered equivalent (i.e., the average symmetry is C<sub>3v</sub>, with the unique methyl group anti to Si-H). In the ESS mechanism, two of the three pairwise interactions between *tert*-butyl groups involve net disrotation; the third interaction involves net conrotation. By this mechanism, all three methyl sites are equivalenced by successive rearrangements in which a given *tert*-butyl group passes through *S* and *E* conformations, e.g., by a succession of the

mode-equivalent *ESS*, *SES*, and *SSE* processes.

To confirm the magnitude of the calculated barriers, we recorded the temperature dependent 25.2 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra<sup>19</sup> of **1**<sup>20</sup> in 4:1  $\text{CF}_2\text{Cl}_2/\text{CF}_3\text{Br}$ . At  $-140^\circ\text{C}$  the singlet due to the methyl carbons ( $\delta_{\text{Me}_4\text{Si}}$  31.0 ppm at  $-70^\circ\text{C}$ ) splits into two singlets in a ratio of  $\sim 2:1$  ( $\delta$  32.3 and 26.4 ppm at  $-157^\circ\text{C}$ , respectively). The corresponding value of  $\Delta G_c^\ddagger$ ,  $6.1 \pm 0.3$  kcal/mol,<sup>21</sup> is in good agreement with the barrier of 6.8 kcal/mol calculated by the EFF method.<sup>23</sup> The observation of two resonance signals is in accord with our calculations which indicate that the (nonobserved) threshold mechanism (*SSS*) for this compound averages two of the three methyl environments at lower temperatures.<sup>24</sup>

The above analysis may be extended to any system of the type *t*- $\text{Bu}_3\text{MX}$ . Thus, besides the obvious analogies to other silanes,<sup>25</sup> the observed coalescences in tri-*tert*-butylphosphines<sup>26</sup> might similarly be explained by a process involving correlated rotation.<sup>27</sup>

Further discussion is reserved for the detailed account of this work.

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- calculations<sup>10</sup> and by electron diffraction,<sup>11</sup> respectively. For *t*- $\text{Bu}_3\text{P}$ , values for  $\phi$  of  $\sim 36$  and  $46^\circ$  have been found by CNDO/2 calculations<sup>12a</sup> and by electron diffraction,<sup>12b</sup> respectively. All of these stereochemically correspondent<sup>13</sup> structures represent examples of static gearing;<sup>3</sup> i.e., a methyl group on one *tert*-butyl group fits between the methyl "teeth" of an adjacent *tert*-butyl, resulting in a "geared", chiral ( $C_2$ ) structure.
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## Chemically Modified Electrodes. 11. Predictability of Formal Potentials of Covalently Immobilized Charge-Transfer Reagents

Sir:

This research in covalent anchoring of redox reagents<sup>1</sup> to electrode surfaces<sup>1</sup> examines the correspondence between electrochemical properties of an immobilized reagent and its solution analogue. Good correspondence is desired for predictive design of electrocatalytic systems.<sup>1b,2</sup>

Predictability of the electrochemical step I and the chemical step II can be scrutinized separately. While developing a diverse chemistry useful for covalently immobilizing OX/RED couples, we have measured a sufficiently extensive series of

