

Experimental and Theoretical Studies of the Rate of *tert*-Lutyl Rotation in 2-*tert*-Butyl-1,3-diheteroatomic Rings. The *gem*-Dialkyl Effect, Ring Geometry, and Lone Pair Orientation as Factors in Conformational Dynamics

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Abstract: Examination of the ¹H dnmr spectra has revealed barriers to *tert*-butyl rotation in 2-*tert*-butyl-2-methyl-1,3-dithiane ($\Delta H^\ddagger = 9.9 \pm 0.3$ kcal/mol, $\Delta S^\ddagger = 1.4 \pm 2.0$ eu, $\Delta G^\ddagger = 9.6 \pm 0.1$ kcal/mol at -83.5°), 2-*tert*-butyl-2-methyl-1,3-dioxane ($\Delta H^\ddagger = 8.9 \pm 0.3$ kcal/mol, $\Delta S^\ddagger = 1.4 \pm 2.0$ eu, $\Delta G^\ddagger = 8.7 \pm 0.1$ kcal/mol at -109.8°), 2-*tert*-butyl-2-methyl-1,3-dithiolane ($\Delta H^\ddagger = 11.1 \pm 0.3$ kcal/mol, $\Delta S^\ddagger = 2.5 \pm 2.0$ eu, $\Delta G^\ddagger = 10.6 \pm 0.1$ kcal/mol at -70.2°), 2-*tert*-butyl-1,3-dithiolane ($\Delta H^\ddagger = 7.5 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = 0.3 \pm 2.0$ eu, $\Delta G^\ddagger = 7.5 \pm 0.2$ kcal/mol at -133.2°), 2-*tert*-butyl-2-methyl-1,3-dioxolane ($\Delta H^\ddagger = 7.5 \pm 0.3$ kcal/mol, $\Delta S^\ddagger = 0 \pm 2.0$ eu, $\Delta G^\ddagger = 7.5 \pm 0.1$ kcal/mol at -124.7°), 2-*tert*-butyl-2-methyl-1,3-oxathiolane ($\Delta H^\ddagger = 10.8 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = 5.5 \pm 5.0$ eu, $\Delta G^\ddagger = 9.8 \pm 0.2$ kcal/mol at -101.2°), and 2-*tert*-butyl-1,3-oxathiolane ($\Delta H^\ddagger = 6.9 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = -1.1 \pm 2.0$ eu, $\Delta G^\ddagger = 7.0 \pm 0.2$ kcal/mol at -139.6°). For 2-*tert*-butyl-1,3-dithiane, 2-*tert*-butyl-1,3-dioxane, and 2-*tert*-butyl-1,3-dioxolane, no clean *tert*-butyl peak separation was observed to -160° . The *tert*-butyl rotational barriers can be rationalized on the basis of ring geometry, lone pair orientation, the *gem*-dialkyl effect, and van der Waals radii. Nonempirical molecular orbital (NEMO) calculations predict the observed barrier sequence consistent with the postulated rationale.

Information regarding the rate of rotation about single bonds and associated rotamer preferences is important in assessing the feasibility of stereospecific chemical synthesis as well as the separation of pure conformers.² Although significant experimental³ and theoretical⁴ efforts have been expended to elucidate the origins of potential barriers to single bond rotation, an incisive depiction of the rate process is elusive even in the case of ethane.⁵

Dynamic nuclear magnetic resonance (dnmr)⁶ studies of *tert*-butyl rotation in a variety of compounds³ have revealed interesting trends regarding the dynamics of single bond rotation. Although ring⁷ and substituent⁸ conformational preferences have been determined for a large variety of six-membered heterocycles, very little

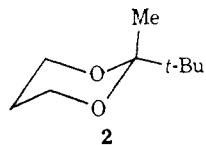
information has been forthcoming regarding the conformational dynamics (e.g., bond rotation) of groups bonded to the heterocyclic system.⁹

This report concerns a dnmr study of *tert*-butyl rotation in a variety of 2-*tert*-butyl-1,3-diheteroatomic 5- and 6-rings with some expected and unexpected observations.

Results and Discussion

Examination of the ¹H dnmr spectrum (60 MHz) of 2-*tert*-butyl-2-methyl-1,3-dioxane (**1**; 5% by weight in CH₂CHCl) at -30° revealed two sharp singlet resonances due to the 2-*tert*-butyl ($\delta 0.94$; 9 H) and 2-methyl ($\delta 1.33$; 3 H) groups which are upfield from the bulk of the ring protons signals. As the temperature was lowered, the 2-methyl resonance remained sharp to -140° except for some slight viscosity broadening (Figure 1). However, at low temperatures, the *tert*-butyl resonance exhibited exchange broadening and under conditions of slow exchange on the dnmr time scale separated into two singlets at $\delta 1.00$ (3 H) and 0.90 (6 H), as illustrated in Figure 1.

Such dnmr spectral changes are best rationalized in terms of slowing *tert*-butyl rotation in **1** on the dnmr time scale at low temperatures. The large steric bulk of *tert*-butyl will lock the ring of **1** into an essentially exclusive preference for the chair conformation with equatorial 2-*tert*-butyl and axial 2-methyl groups (**2**).⁸



Considering a Newman projection of **2** looking down the bond between the central *tert*-butyl carbon and the

(9) C. H. Bushweller, G. U. Rao, W. G. Anderson, and P. E. Stevenson, *J. Amer. Chem. Soc.*, **94**, 4743 (1972).

(1) Alfred P. Sloan Research Fellow, 1971-1974; Camille and Henry Dreyfus Teacher-Scholar, 1972-present.

(2) C. H. Bushweller, J. Golini, G. U. Rao, and J. W. O'Neil, *J. Amer. Chem. Soc.*, **92**, 3055 (1970); F. R. Jensen and C. H. Bushweller, *ibid.*, **91**, 3223 (1969).

(3) (a) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *Tetrahedron*, **27**, 5761 (1971); C. H. Bushweller and W. G. Anderson, *Tetrahedron Lett.*, 129 (1972); C. H. Bushweller, W. G. Anderson, J. W. O'Neil, and H. S. Bilofsky, *ibid.*, 717 (1973); C. H. Bushweller, W. J. Dewkett, J. W. O'Neil, and H. Beall, *J. Org. Chem.*, **36**, 3782 (1971); (b) R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, **43**, 602 (1965); C. H. Bushweller and W. G. Anderson, *Tetrahedron Lett.*, 1811 (1972); J. E. Anderson and H. Pearson, *J. Chem. Soc. B*, 1209 (1971); B. L. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 4472 (1971); H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970); (c) C. H. Bushweller, J. A. Brunelle, W. G. Anderson and H. S. Bilofsky, *Tetrahedron Lett.*, 3261 (1972); C. H. Bushweller and J. A. Brunelle, *J. Amer. Chem. Soc.*, **95**, 5949 (1973).

(4) J. P. Lowe, *Science*, **179**, 527 (1973); E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959); J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968); R. A. Petrick and E. Wyn-Jones, *Quart. Rev., Chem. Soc.*, **23**, 301 (1969).

(5) I. R. Epstein and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **92**, 6094 (1970), and references therein.

(6) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

(7) (a) C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4**, 39 (1967); (b) C. H. Bushweller, G. U. Rao, and F. H. Bissett, *J. Amer. Chem. Soc.*, **93**, 3058 (1971), and references therein.

(8) (a) E. L. Eliel, *Accounts Chem. Res.*, **3**, 1 (1970); (b) C. H. Bushweller, *Int. J. Sulfur Chem., Part C*, **5**, 75 (1970).

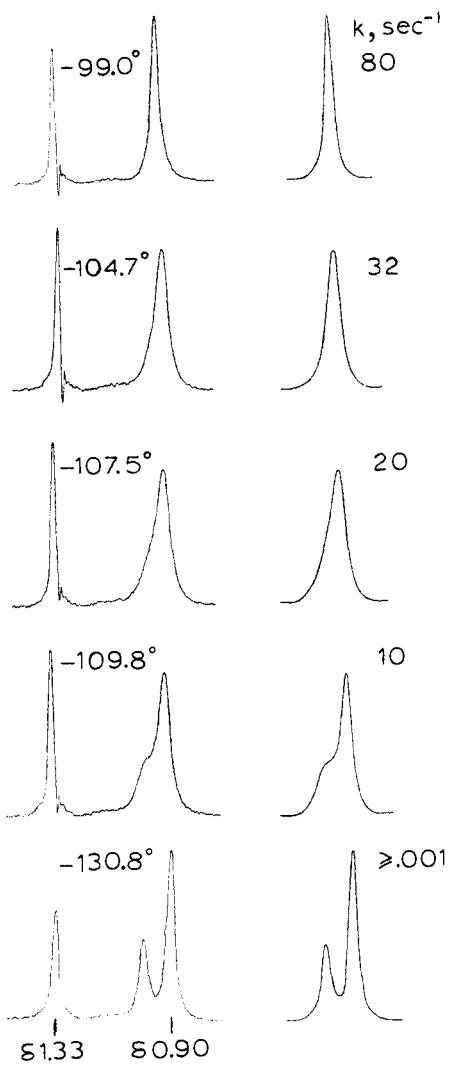
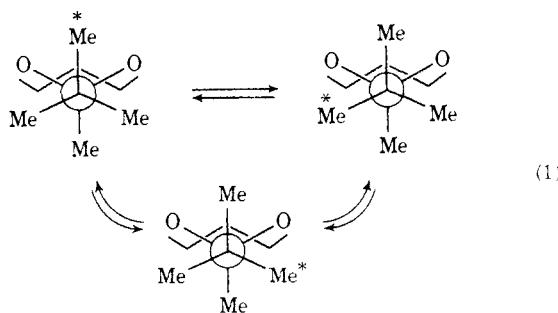


Figure 1. The experimental ^1H dnmr spectra (60 MHz) of the 2-methyl and 2-tert-butyl resonances of 2-tert-butyl-2-methyl-1,3-dioxane (5% by weight in CH_2CHCl) and theoretical spectra calculated as a function of the rate of *tert*-butyl rotation (k = first order rate constant for the disappearance of a methyl group from any one of the three sites on *tert*-butyl).

2-carbon of the ring (eq 1), it is clear that under condi-



tions of slow *tert*-butyl rotation there should be two resonances corresponding to two equivalent *tert*-butyl methyls gauche to the 2-methyl group and one different methyl gauche to the two oxygens as observed (Figure 1).

Taking precautions described in previous dnmr studies in order to minimize systematic errors,¹⁰ theo-

(10) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *Tetrahedron*, **28**, 2697 (1972).

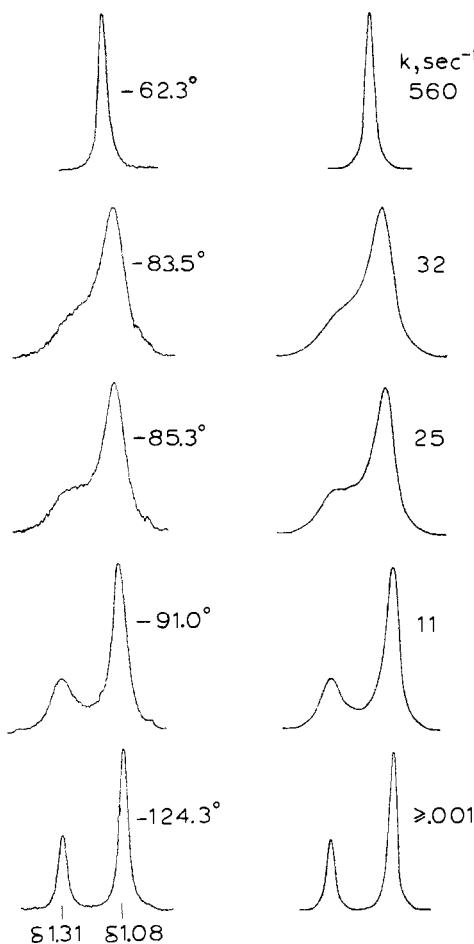


Figure 2. Experimental ^1H dnmr spectra (60 MHz) of the 2-*tert*-butyl group of 2-*tert*-butyl-2-methyl-1,3-dithiane (5% by weight in CH_2CHCl) and spectra calculated as a function of the rate of *tert*-butyl rotation (k = first order rate constant for the disappearance of a methyl group from any one of the three sites on *tert*-butyl).

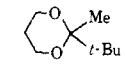
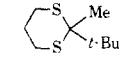
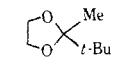
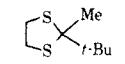
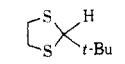
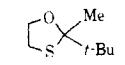
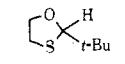
retical ^1H dnmr spectra were generated¹¹ as a function of the rate of *tert*-butyl rotation, and the derived activation parameters for *tert*-butyl rotation are compiled in Table I. Slow exchange chemical shift values for the nonequivalent *tert*-butyl methyl groups are also listed in Table I.

Similar dnmr spectral behavior is observed for the *tert*-butyl resonance of 2-*tert*-butyl-2-methyl-1,3-dithiane (**3**; 5% by weight in CH_2CHCl ; Figure 2) consistent with slowing *tert*-butyl rotation on the dnmr time scale in a conformation analogous to **2**. One significant dnmr spectral deviation between **1** and **3** is a markedly larger chemical shift difference between the nonequivalent methyls of *tert*-butyl in **3** [δ 1.31 (3 H); δ 1.08 (6 H); Figure 2] as compared to **1** [δ 1.00 (3 H); δ 0.90 (6 H); Figure 1]. Theoretical *tert*-butyl dnmr spectra were calculated for **3** as a function of the rate of *tert*-butyl rotation in a manner exactly analogous to that for **1** and the derived activation parameters are compiled in Table I.

The ^1H dnmr spectrum of the *tert*-butyl group of 2-*tert*-butyl-2-methyl-1,3-dioxolane (**4**; 5% by weight in CH_2CHCl) also changed at low temperatures in a manner consistent with slowing *tert*-butyl rotation

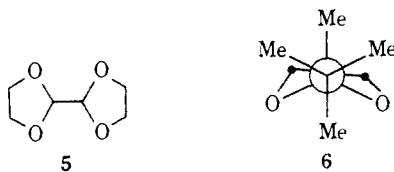
(11) The program used is DNMR3 by D. A. Kleier, G. Binsch, A. Steigel, and J. Sauer, *J. Amer. Chem. Soc.*, **92**, 3787 (1970); Program 165, Quantum Chemistry Program Exchange, Indiana University, 1969.

Table I. Slow Exchange Nmr Chemical Shifts and Activation Parameters for *tert*-Butyl Rotation in 2-*tert*-Butyl-1,3-diheteroatomic Rings

Compd	Chemical shifts of <i>t</i> -Bu at slow exchange, ppm ^c	<i>E_a</i> , kcal/mol	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	ΔG^\ddagger , kcal/mol	
1		1.00 (3 H); 0.90 (6 H) ^a	9.3 ± 0.3	8.9 ± 0.3	1.4 ± 2.0	8.7 ± 0.1 (-109.8°)
3		1.31 (3 H); 1.08 (6 H) ^a	10.3 ± 0.3	9.9 ± 0.3	1.4 ± 2.0	9.6 ± 0.1 (-83.5°)
4		0.97 (6 H); 0.88 (3 H) ^a	7.8 ± 0.3	7.5 ± 0.3	0.0 ± 2.0	7.5 ± 0.1 (-124.7°)
7		1.25 (3 H); 1.08 (6 H) ^a	11.5 ± 0.3	11.1 ± 0.3	2.5 ± 2.0	10.6 ± 0.1 (-70.2°)
8		1.05 (6 H); 0.99 (3 H) ^b	7.9 ± 0.4	7.5 ± 0.4	0.0 ± 3.0	7.5 ± 0.2 (-133.2°)
9		1.05 (3 H); 1.04 (3 H); 1.00 (3 H) ^a	11.1 ± 0.4	10.8 ± 0.4	5.5 ± 4.0	9.8 ± 0.1 (-101.2°)
10		1.08 (3 H); 0.94 (3 H); 0.91 (3H) ^b	7.1 ± 0.4	6.9 ± 0.4	-1.1 ± 2.0	7.0 ± 0.2 (-139.6°)

^a 5% by weight in CH₂CHCl. ^b 5% by weight in CBrF₃. ^c Relative to tetramethylsilane.

(Figure 3; Table I). By analogy with available X-ray crystallographic data for 2,2'-bis-1,3-dioxolane (**5**) in-



dicating a 5-ring geometry midway between half-chair (*C*₂ symmetry) and envelope (*C*_s symmetry) forms,¹² a minimum potential geometry similar to **6** may be assumed for 2-*tert*-butyl-2-methyl-1,3-dioxolane (Newman projection looking down the bond between the central *tert*-butyl carbon and the 2-carbon of the ring). It must be stated at this point that the very small energy difference between a variety of 5-ring conformations and a presumed low barrier to 1,3-dioxolane ring pseudorotation¹³ preclude a quantitatively unequivocal assignment of ring geometry in **4**.¹⁴ In any event, fast ring stereomutation and slow *tert*-butyl rotation on the dnmr time scale will lead to two singlet resonances of relative intensities 2:1 for *tert*-butyl as observed at -145.0° (Figure 3). It is interesting to note a reversal of chemical shift trend for the two *tert*-butyl peaks in **4** (-145.0°; Figure 3) in which the methyl group gauche to the two oxygens (**6**) now gives a signal upfield from that due to the other two methyls gauche to the 2-methyl which is reversed from the situation in **1** (Figure 1) and **3** (Figure 2). Activation pa-

rameters for *tert*-butyl rotation in 2-*tert*-butyl-2-methyl-1,3-dioxolane (Table I) were calculated using the procedure described previously.

Examination of the ¹H dnmr spectra of the *tert*-butyl group in 2-*tert*-butyl-2-methyl-1,3-dithiolane (**7**), 2-*tert*-butyl-1,3-dithiolane (**8**), 2-*tert*-butyl-2-methyl-1,3-oxathiolane (**9**), and 2-*tert*-butyl-1,3-oxathiolane (**10**) also revealed changes consistent with slowing *tert*-butyl rotation. In the cases of **9** and **10**, it was necessary to employ three chemical shifts for *tert*-butyl at slow and intermediate exchange to obtain fits of the theoretical to experimental dnmr spectra. In each case (**9** and **10**), two of the assumed chemical shifts are so close as to preclude resolution in the slow exchange dnmr spectra. The pertinent dnmr and activation parameters are compiled in Table I.

Perusal of Table I reveals expected trends in the rate of *tert*-butyl rotation and an interesting trend reversal. Comparison of the barriers to *tert*-butyl rotation (Table I) of **7** and **8** or **9** and **10** indicates the not unexpected result that methyl is substantially more hindering to *tert*-butyl rotation than hydrogen. Comparison of **1** and **3** or **4** and **7** indicates also that sulfur is apparently more hindering to *tert*-butyl rotation than oxygen which is consistent with a greater *A* value for SCD₃ (1.07 kcal/mol at -79°)¹⁵ as compared to OCD₃ (0.55 kcal/mol at -82°)¹⁵ as well as a greater van der Waals radius for sulfur.

However, in proceeding from **1** to **4** (Table I), one observes a significant reduction in the barrier to *tert*-butyl rotation, while going from **3** to **7** the barrier increases. Indeed, in light of the difference between the

⁽¹²⁾ S. Furberg and O. Hassel, *Acta Chem. Scand.*, **4**, 1584 (1950).⁽¹³⁾ J. Laane, *Quart. Rev., Chem. Soc.*, **25**, 553 (1971).⁽¹⁴⁾ C. Altona and A. P. M. van der Veen, *Tetrahedron*, **24**, 4377 (1968).⁽¹⁵⁾ F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Amer. Chem. Soc.*, **91**, 344 (1969).

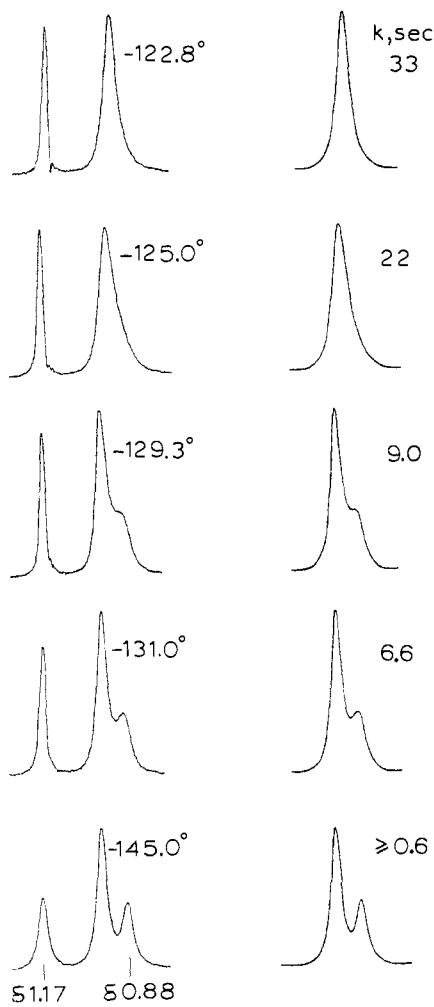
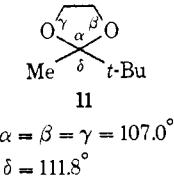


Figure 3. The experimental ^1H NMR spectra (60 MHz) of the 2-methyl and 2-tert-butyl groups of 2-tert-butyl-2-methyl-1,3-dioxolane (5% by weight in CH_2Cl_2) and theoretical spectra calculated as a function of the rate of *tert*-butyl rotation (k = first order rate constant for the disappearance of a methyl group from any one of the three sites on *tert*-butyl).

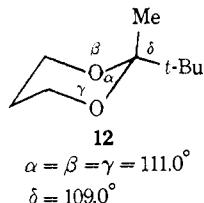
barriers in **1** and **3**, the much larger difference between **4** and **7** is remarkable.

In considering results obtained for *tert*-butyl rotation in *tert*-butylcyclopentane ($\Delta G^\ddagger = 6.0$ kcal/mol at -155°), *tert*-butylcyclohexane ($\Delta G^\ddagger = 6.3$ kcal/mol at -150°), and *tert*-butylcycloheptane ($\Delta G^\ddagger = 7.4$ kcal/mol at -126°),¹⁶ the barrier sequence for **1** and **4** seems normal. As demonstrated by vector analysis, incorporation of the two oxygen atoms into the 5-ring of **4** results in a significant pinning back of the oxygen atoms in **4** as compared to **1** leading to a decrease in the O-C-O bond angle in **4** and a concomitant increase in the *t*-Bu-C-Me bond angle (*gem*-dialkyl effect).¹⁷ The net effect of these conformational adjustments is to move the 2-methyl group and oxygen atoms of **4** farther away from the *tert*-butyl methyls and lower the barrier as compared to **1**. Nonempirical molecular orbital (NEMO) calculations^{18,19} performed in this

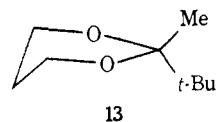
laboratory substantiate the observed sequence for **1** and **4**. Using the distorted envelope conformation (**6**) for **4** with a C-O bond length of 1.43 Å, a C-C bond length of 1.55 Å, a dihedral angle between O(1), C(2) and C(4), C(5) of 14° and between C(2), O(3) and C(4), C(5) of -28° ,^{7a} and bond angles as in **11**, a barrier to



tert-butyl rotation of 24.2 kcal/mol is calculated. For **1**, an initial calculation employing a fully staggered perfect chair form (dihedral angles of 63 and -63°)^{7a} and bond angles as in **12** gave a barrier to *tert*-butyl rotation



of 27.1 kcal/mol consistent with the observed experimental trend (Table I). However, in light of previous data for 2-substituted-1,3-dioxanes indicating severe 1,3-nonbonded repulsions involving the axial methyl of **12**,⁸ a flattening of the O-C-O portion of the ring in **12** would be expected. Indeed, the NEMO calculations indicate a substantial energy decrease (~ 25 kcal/mol) as compared to the perfect chair form (**12**) by tilting the angle defined by the planes of the O(1), C(2), O(3) and O(2), C(3), O(1), C(5) atoms half way toward the semiplanar conformation (**13**). Although a stabilization of



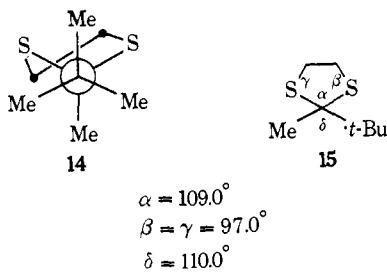
the system occurs as a result of the tilt, the calculated barrier to *tert*-butyl rotation increases to 27.7 kcal/mol. This observation is important in subsequent discussion.

In considering the trend reversal for **3** and **7** (Table I) as compared to **1** and **4**, going to a *half-chair* conformation for the 5-ring in **7** from a 6-ring in **3** actually requires a greater differential pinning back of the two sulfur atoms than for the oxygen atoms in proceeding from **1** to **4**. Obviously, the *gem*-dialkyl effect cannot be invoked as a dominant factor in the sequence **3** and **7**. Calculation of the barrier to *tert*-butyl rotation in **7** using the NEMO method and employing a *half-chair* geometry (**14**) as indicated from X-ray crystallographic data for 2,2'-bis-1,3-dithiolane²⁰ and solution NMR studies of various 1,3-dithiolanes²¹ with a C-S bond length of 1.82 Å, a dihedral angle between S(1), C(2) and C(4), C(5) of 11° and between S(3), C(2) and C(4), C(5) of 15° , and bond angles as in **15** gave a value of

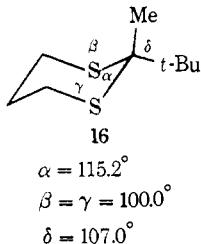
(19) Cartesian coordinates for these calculations were obtained through the use of the program "COORD (time sharing version)," P. E. Stevenson and J. E. Merrill, Quantum Chemistry Program Exchange, No. 186.

(20) L. B. Brahde, *Acta Chem. Scand.*, **8**, 1145 (1954).

(21) L. A. Sternson, D. A. Covello, and R. S. Egan, *J. Amer. Chem. Soc.*, **93**, 6529 (1971).



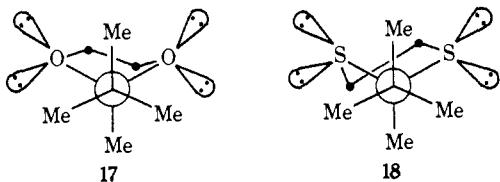
51.6 kcal/mol. Using the geometry of the 1,3-dithiane ring determined from the X-ray crystallographic study of 2-phenyl-1,3-dithiane²² employing the bond angles in 16, the barrier to *tert*-butyl rotation is calculated to be



49.1 kcal/mol. Tilting the S-C-S fragment of 16 half way toward a semiplanar conformation produced only a small decrease in energy (~ 5 kcal/mol) and a significant increase in the barrier to *tert*-butyl rotation (55.7 kcal/mol). It would seem that there exists little tendency for the 1,3-dithiane ring in 3 to flatten toward a semiplanar form as compared to 1. Again, as in 1, a flattening of the ring in 3 would *increase* the barrier to *tert*-butyl rotation compared to the perfect chair form.

Thus, assuming a flattened ring geometry for 1, essentially a perfect chair form for 3, a twisted envelope ring for 4, and a half-chair for 7 produces the correct barrier trend reversal theoretically, although the calculated values are obviously too high.

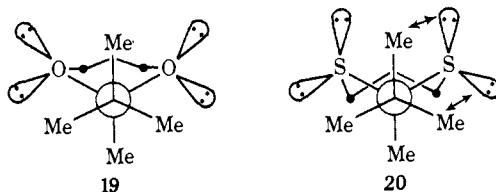
Since the degree of pinning back of the two heteroatoms in 4 and 7 is significant, *i.e.*, the *gem*-dialkyl effect is operative in both cases, the trend reversal for 1 and 4 *vs.* 3 and 7 must be due to some other phenomenon. In the case of 4 and 7, the dihedral angles associated with the rings are quite small leading to a relatively small degree of puckering. If one assumes a *directional character* for the lone pairs of electrons on oxygen or sulfur, the net result of such ring geometries is a skewing of the lone pairs away from a parallel 1,3-*syn*-axial orientation with the methyl groups of staggered *tert*-butyl (17 and 18). The apparently strong



tendency for the O-C-O fragment of 1 to tilt toward a semiplanar form would also create a local environment

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about *tert*-butyl (19) similar to 17 and 18. In contrast, the minimal tendency toward flattening of the ring in 3 says that all of the *tert*-butyl methyls are essentially *syn*-axial to the sulfur lone pairs (20). This *syn*-



axial bond pair-lone pair repulsion in 20 should serve to destabilize 20. In the eclipsed transition state for *tert*-butyl rotation in 2-*tert*-butyl-2-methyl-1,3-dithiane, the *syn*-axial bond pair-lone pair repulsions in 20 are relieved. In 17, 18, and 19, rotation of the *tert*-butyl group toward an eclipsed form serves to *increase* such C-C bond pair-lone pair repulsions. Thus, in 17, 18, and 19, bond pair-lone pair repulsions would serve to destabilize the transition state for *tert*-butyl rotation and raise the barrier, while in 3, such repulsions would destabilize the ground state (20) and lower the barrier. The fact that the geometric arrangement of *tert*-butyl methyls and sulfur lone pairs in 3 is different from that in 7 provides a rationale in terms of the above discussion for the barrier in 7 being higher than in 3. The similar orientation of *tert*-butyl methyls and oxygen lone pairs in 1 and 4 indicates that the effect of bond pair-lone pair repulsions during the *tert*-butyl rotational itinerary should be very similar in both cases. The substantially lower barrier in 4 as compared to 1 attests to the dominance of the *gem*-dialkyl effect in these two compounds and possibly to less directional (or nondirectional²³) character for the oxygen lone pairs as compared to sulfur.

A rationale of unusual conformational preferences in a series of *s*-tetrathianes has been presented also in terms of directional sulfur lone pairs.^{7b,24}

The barriers to *tert*-butyl rotation in the 1,3-oxathiolanes 9 and 10 are essentially predictable on the basis of the above discussion with the higher barrier in 9 consistent with a more hindering 2-methyl group.

Experimental Section

The nmr spectra were obtained using a Varian HR-60A spectrometer equipped with a custom-built variable-temperature probe.²⁵ Spectral calibrations were performed by the audiomodulation technique using a Hewlett-Packard 651-A audiooscillator and 5221B electronic counter.

The various 1,3-dithianes, 1,3-dioxanes, and 1,3-oxathiolanes were prepared by reaction of the appropriate diol, dithiol, or mercaptoalcohol with pivaldehyde or *tert*-butyl methyl ketone in the presence of *p*-toluenesulfonic acid.^{8a} All spectral data and elemental analyses are consistent with the molecular structures.

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