nearly coplanar than those in [14]annulene and had different patterns of deviations from the best plane.[13]

The distortions from planarity are distributed throughout the molecule. With the exception of the C(6)–C(7) bond, the torsion angles around the crystallographically independent half of the ring lie in the range of 10–20° (for cis bonds) and 160–170° (for trans bonds); the substituents on the C(6) and C(7) atoms are almost completely eclipsed (torsion angle = −1.5°).

The structure found herein is entirely compatible with the nmr spectrum obtained at low temperatures (a peak corresponding to four protons at τ 10.61 and a ten proton peak at τ 2.12, at −126°) for freshly dissolved [14]annulene;[8,9] an "isodynamic mobility"[9] among conformations of type I is responsible for the equivalence of all the protons at higher temperatures. Our results emphasize the need to recognize and make allowance for the high degree of nonplanarity in this $[4n + 2]$annulene when calculations of resonance energy are being made,[2] and provide a basis for such calculations.[14]

Acknowledgment. We thank Professor Franz Sondheimer and Dr. Klaus Stöckel for generously supplying us with the sample of [14]annulene.

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(13) It should be pointed out that as both [14]- and [18]annulene, IIIa and IIIb, occupy sites with crystallographic centers of symmetry, it is possible that effects arising from disorder could mask certain minor differences in bond length. No obvious evidence for disorder was found in the crystallographic studies on these molecules.

(14) The list of atomic coordinates and structure amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number JACS-72-4741. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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The Rate of *tert*-Butyl Rotation in 2-*tert*-Butyl 1,3-Diheteroatomic Rings. The Roles of Bond Angle and Bond Length in a Trend Reversal

Sir:

Knowledge regarding the dynamics of rotation about single bonds and conformational preference has implications in both mechanistic and synthetic chemistry. Although significant experimental[1] and theoretical[2] efforts have been expended to elucidate the origin of the potential barriers to rotation about single bonds, an incisive depiction of the barrier origin(s) is elusive even in the case of ethane.[3]

This report concerns the measurement of the rate of *tert*-butyl rotation in a series of 2-*tert*-butyl 1,3-diheteroatomic rings (1–7; Table I) indicating not only an expected dependence on the steric bulk of proximate alkyl groups and heteroatoms but also a significant dependence on the preferred geometry of the heterocycle involved.[4]

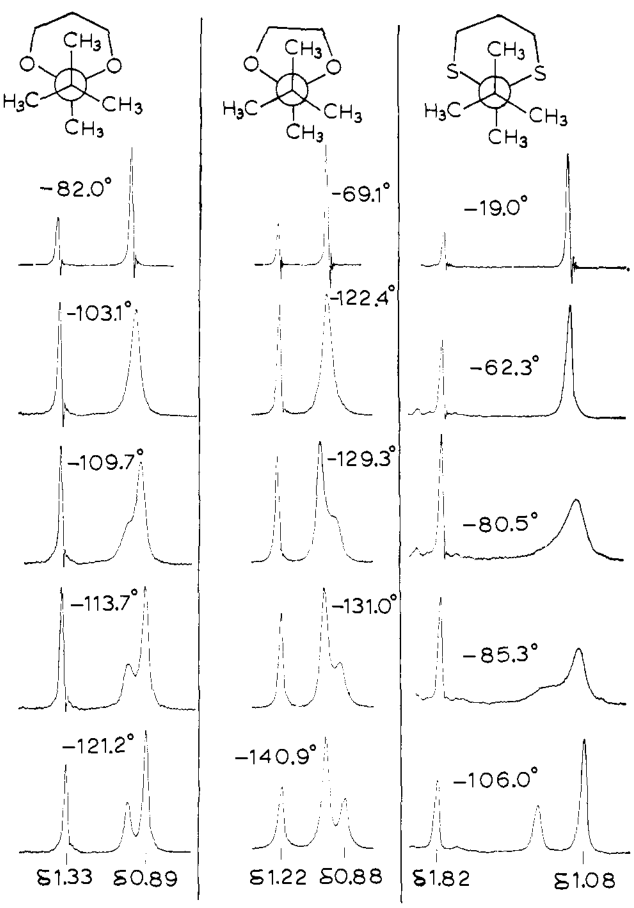
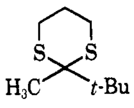
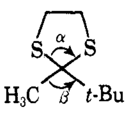


Figure 1. The ^{1}H dnmr spectrum (60 MHz) of **6**, **7**, and **1** as a function of temperature.



1



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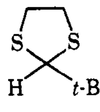

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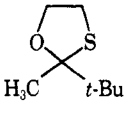

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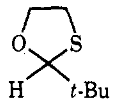

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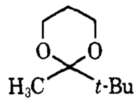

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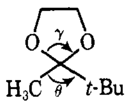

7

Examination of the ^{1}H dnmr[5] spectrum (60 MHz) of **1**–**7** revealed in all cases changes in the *tert*-butyl resonance attributable to slowing of *tert*-butyl rotation. Three cases (**1**, **6**, **7**) are illustrated in Figure 1. The slow exchange chemical shifts of the methyl groups of each *tert*-butyl group (Table I) were obtained from a total line-shape analysis. Also compiled in Table I are activation parameters for *tert*-butyl rotation in **1**–**7** derived from total line-shape analyses.[6] Unfortunately, examination of the ^{1}H dnmr spectrum of 2-*tert*-butyl-1,3-dithiane, 2-*tert*-butyl-1,3-dioxane, and 2-*tert*-butyl-1,3-dioxolane revealed only broadening of the *tert*-butyl resonance with no clean peak separation at low temperatures.

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Table I. Nmr and Activation Parameters for *tert*-Butyl Rotation in 2-*tert*-Butyl 1,3-Diheteroatomic Rings

Compd	Chemical shifts of *t*-Bu peaks at slow exchange, Hz, 60 MHz	$\Delta G^{\ddagger}$, kcal/mol (temp, °C)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1[a]	65.1 (6 H), 78.8 (3 H)	9.6 ± 0.1 (−83.5)	9.9 ± 0.3	1.4 ± 2.0
2[b]	75.0 (3 H), 65.0 (6 H)	10.6 ± 0.1 (−70.2)		
3[b]	63.1 (6 H), 59.1 (3 H)	7.5 ± 0.2 (−133.2)		
4[b]	62.8 (3 H), 62.3 (3 H), 59.7 (3 H)	9.8 ± 0.1 (−101.2)		
5[b]	65.0 (3 H), 56.5 (3 H), 54.5 (3 H)	7.0 ± 0.2 (−139.6)		
6[a]	60.5 (3 H), 54.2 (6 H)	8.7 ± 0.1 (−109.8)		
7[b]	58.5 (6 H), 52.6 (3 H)	7.5 ± 0.1 (−124.7)	7.5 ± 0.3	0 ± 2.0

[a] 5% v/v in CH_2CHCl. [b] 5% v/v in $CBrF_3$.

Perusal of Table I reveals some expected and some unusual trends. First, we have completed the line-shape analysis at several temperatures for **1** and **7** revealing very small entropies of activation ($\Delta S^{\ddagger}$) for *tert*-butyl rotation. Thus, it may be assumed in this series that the free energy of activation ($\Delta G^{\ddagger}$) is a good estimate of the enthalpy of activation ($\Delta H^{\ddagger}$) for *tert*-butyl rotation. The higher barriers to *tert*-butyl rotation in **2** and **4** as compared to **3** and **5**, respectively, are clearly consistent with not unexpected increased non-bonded repulsions in the eclipsed transition state involving methyl as compared to hydrogen. The barriers to *tert*-butyl rotation for the two essentially strain-free 6-rings (**1**, **6**) reveal sulfur to be more effective than oxygen in hindering *tert*-butyl rotation. This observation obviously could be rationalized by the larger van der Waals radius for sulfur leading to enhanced repulsions in **1** as compared to **6** in the eclipsed transition state and is consistent with a greater preference of sulfur for the equatorial *vs.* the axial position in monosubstituted cyclohexanes, *e.g.*, SCD_3 ($\Delta G°_{ae} = -1.07$ kcal/mol at −79°)[7] and OCD_3 ($\Delta G°_{ae} = -0.55$ kcal/mol at −82°).[7] However, the higher barrier in **1** as compared to **6** could also be due in part to a larger SCS angle (*ca.* 115°)[8] in **1** rendering the sulfurs in close proximity to *tert*-butyl in **1** as compared to **6** in which the OCO angle (*ca.* 111°) is smaller.[9]

Ostensibly, the nonbonded repulsions hindering *tert*-butyl rotation should be similar in **6** and **7**, but the barrier in **7** is significantly lower than that in **6**. Whether one assumes the 5-ring conformation in **7** to be the half-chair or envelope,[4] examination of models and vector analysis indicate that incorporation of the CH_2CH_2 fragment into the 5-ring requires a "pinning back" of the oxygen atoms, *i.e.*, a closing of the angle γ in **7** as compared to the OCO angle in **6**. A corollary effect to the closing of the angle γ in **7** is an opening of the angle θ in **7** (geminal dialkyl effect[10]). The net result of these bond angle adjustments is to move the oxygen atoms and methyl group in **7** further away from *tert*-butyl and lower the barrier as compared to **6**. This trend is analogous to *tert*-butyl rotation in *tert*-butylcyclopentane ($\Delta G^{\ddagger} \sim 6.0$ kcal/mol at −155°),[11] *tert*-butylcyclohexane ($\Delta G^{\ddagger} \sim 6.3$ kcal/mol at −150°),[11] and *tert*-butylcycloheptane ($\Delta G^{\ddagger} = 7.4$ kcal/mol at −126°).[11] A similar analysis of **2** indicates that despite the smaller preferred CSC bond angle (100°)[8] and longer C–S bond length (1.82 Å)[8] as compared to the preferred COC bond angle (111°)[9] and shorter C–O bond length (1.43 Å),[9] there results a pinning back of the sulfur atoms in the preferred half-chair form of **2**[4] to an even greater extent than the oxygen atoms in **7**. Presumably, this would lead to bond angle adjustments (α and β in **2**) analogous to those in **7**. However, the "anomalously" higher barrier in **2** as compared to **1** is a reversal of the trend in **6** and **7** as well as in the *tert*-butylcycloalkanes. The rationale for this behavior is not totally clear. Predictably, the barrier to *tert*-butyl rotation in **4** is between **2** and **7**.

Thus, it is clear that conformational adjustments in rings dictated by bond angle and bond length requirements can have a profound and not necessarily consistent effect on the conformational dynamics of attached substituents.

Acknowledgment. We are grateful to the National Science Foundation (GP-18197) for support and to Dr. S. J. Weininger for stimulating suggestions.

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Hydrogen-Bonded Complex Formation as Evidenced by Solvatochromic Shifts

Sir:

Enhanced bathochromic shifts for 4-nitroaniline (**1**) relative to *N*,*N*-diethyl-4-nitroaniline (**2**) [$-\Delta\Delta\nu$(**1**–**2**)] and for 4-nitrophenol (**3**) relative to 4-nitroanisole (**4**) [$-\Delta\Delta\nu$(**3**–**4**)] on going from cyclohexane to a series of alcohol solvents have been represented[1] as arising from hydrogen bonding *by* **1** and **3** *to* the alcohols, with the magnitudes of the $-\Delta\Delta\nu$ values considered to be measures of relative solvent proton affinities. Good linear correlations were noted between the $-\Delta\Delta\nu$ values and σ^* values of R in ROH.

We wish now to report that, on going from cyclohexane to a number of non-self-associating solvents of various types, $-\Delta\Delta\nu$(**1**–**2**) and $-\Delta\Delta\nu$(**3**–**4**) values show good linear correlation with pK_{HB} values (logarithms of formation constants)[2] and excellent linear correlation with Δ values (limiting F nmr shifts)[3] for hydrogen-

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