Conformational Analysis. X. Chair–Twist Energy Difference in 1,3-Oxathianes[1a]

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Several recent reports[2] have dealt with the chair–twist transformation of 1,3-dioxanes and a paper based on chemical equilibration and ^{1}H nmr spectroscopy has also been published on that of 1,3-dithianes.[3] The chair–twist enthalpy difference of the 1,3-oxathiane ring[4] has been estimated at 25 kJ mol^{-1} (6.0 kcal mol^{-1}) by comparison with the 1,3-dioxane and 1,3-dithiane values. A gas-phase value of 22.5 ± 4.0 kJ mol^{-1} (5.4 ± 1.0 kcal mol^{-1}) has very recently been obtained by use of appearance potentials of the $[M - CH_3]^+$ ions of *cis-* and *trans*-2,2,4,6-tetramethyl-1,3-oxathiane.[5]

The aim of our present study was to determine thermodynamic parameters for the chair–twist change of the 1,3-oxathiane ring by means of chemical equilibration. For this purpose, we selected the diastereoisomeric 2-*tert*-butyl-2,6-dimethyl-1,3-oxathianes, of which the *cis*-2,6-diMe isomer is likely to exist in a twist conformation to avoid the interactions present in a chair conformation, *viz.*, axial *tert*-butyl or syn-axial arrangement of 2 and 6 methyl groups.[2b,4,5]

Results

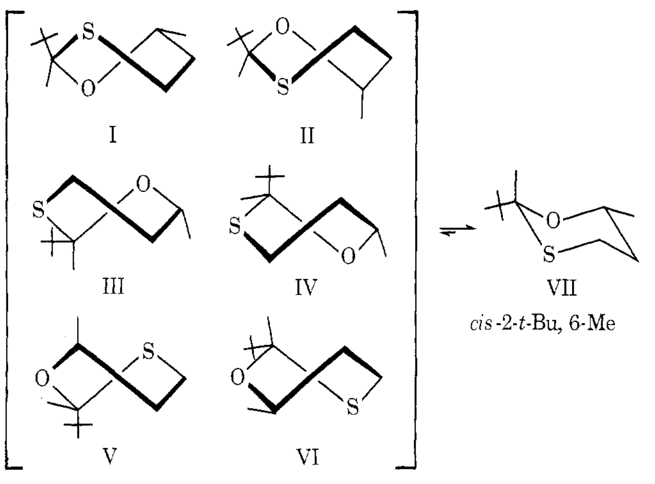
The equilibria were established at 280, 298, and 318°K. The respective equilibrium constants are shown in Table I together with $\Delta H°$ and $\Delta S°$ obtained from them by the method of least squares.

Table I
Equilibria between *r*-2-*tert*-Butyl-2,*trans*-6- and *r*-2-*tert*-Butyl-2,*cis*-6-dimethyl-1,3-oxathianes in 10% (v/v) CCl_4 Solutions

Temp, °K	K = [trans]/[cis][a]	—$\Delta G°$, kJ mol^{-1} (kcal mol^{-1})
280	81.18 ± 7.22[b]	10.241 ± 0.209[b] (2.448)
298	56.97 ± 2.78	10.021 ± 0.121 (2.395)
318	41.15 ± 0.96	9.833 ± 0.059 (2.350)
$-\Delta H°$	13.24 ± 0.14[c] kJ mol^{-1} (3.164 kcal mol^{-1})	
$-\Delta S°$	10.73 ± 0.48[c] J mol^{-1} °K^{-1} (2.564 cal mol^{-1} °K^{-1})	
$-\Delta G°$ (298)	10.04 kJ mol^{-1} (2.40 kcal mol^{-1})	

[a] Glpc area ratios; response ratio assumed to be unity. The values shown are the means of two or three parallel samples, which were analyzed 6–12 times. The systematic error introduced by assuming the response ratio to be unity is likely to be much less than the standard deviation of the measurements. [b] Standard deviations. [c] Statistical errors of the least-squares plot.

Scheme I



cis-2-*t*-Bu, 6-Me

trans-2-*t*-Bu, 6-Me

Discussion

r-2-*tert*-Butyl-2,*trans*-6-dimethyl-1,3-oxathiane has six conceivable twist conformations (I–VI) while the other isomer exists in a single chair conformation (VII) only, excluding enantiomeric forms (Scheme I).

Owing to the pseudo-axial *tert*-butyl groups the contributions of IV and V can be neglected. Inspection of molecular models[6] reveals that I and VI may not differ significantly in energy. Owing to the peculiar geometry of the ring[4] the pseudo-axial methyl group in VI leans appreciably outward. Consequently, the residual interactions due to the isoclinal[7] *tert*-butyl group in I and the "pseudo-axial" methyl group in VI are nearly equal and may not exceed 2 kJ mol^{-1} (0.5 kcal mol^{-1}).

As to the twist forms II and III, they also seem to be nearly equally stable.[6] II has an isoclinal *tert*-butyl group and a pseudo-axial methyl group at position 6, which interacts with the sulfur atom only. III has merely a pseudo-axial methyl group at position 2, which now, however, interacts with the "syn-axial" hydrogen atom at position 5. Both in II and III these nonbonded interactions are likely to be about 4 kJ mol^{-1} (1 kcal mol^{-1}).[3,4,8]

Table II
Chair–Twist Interconversion in Cyclohexane, 1,3-Dioxane, 1,3-Oxathiane, and 1,3-Dithiane

Compd	$\Delta G°_{CT}$, kJ mol^{-1} (kcal mol^{-1})	$\Delta H°_{CT}$, kJ mol^{-1} (kcal mol^{-1})	$\Delta S°_{CT}$, J mol^{-1} °K^{-1} (cal mol^{-1} °K^{-1})	Ref
Cyclohexane[a]	21.2	25.2	13.4	11
	(5.1)	(6.0)	(3.2)	
1,3-Dioxane[b,c]	33.5	35.8	$\lesssim$9.1	11
	(8.0)	(8.6)	($\lesssim$2.2)	
1,3-Oxathiane[d]	23 ± 2	25.2	~9.1	This work
	(5.5)	(6.0)	(~2.2)	
1,3-Dithiane[e]	7.6	14.3	22.3	3
	(1.8)	(3.4)	(5.3)	
	11.0	16.7	19.0	11
	(2.6)	(4.0)	(4.5)	

[a] For the 1,3-di-*tert*-butyl isomer; N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, **82,** 2393 (1960). [b] $\Delta H°_{CT}(g)$ = 35.6 ± 2.1 kJ mol^{-1} (8.5 ± 0.5 kcal mol^{-1}; ref 2e). [c] Values ranging from 26 to 30 kJ mol^{-1} (6.2–7.2 kcal mol^{-1}) have been proposed for $\Delta H°_{CT}$ on the basis of the dependence of geminal (C-2) and vicinal coupling constants on temperature in ref 2i. [d] $\Delta H°_{CT}(g)$ = 25.0 ± 4.0 kJ mol^{-1} (6.0 ± 1.0 kcal mol^{-1}) after a correction for the double-buttressing effect in 2,2,*cis*-4,6-tetramethyl-1,3-oxathiane (ref 5, see text also). [e] See discussion.

If we assume that the excess entropy of the *trans*-2-*t*-Bu-6-Me isomer is principally due to the mixing of the different twist conformations (I–III and VI), the contributions of the different twist forms may be estimated from the experimentally determined entropy difference (10.73 J mol^{-1} °K^{-1} = 2.56 cal mol^{-1} °K^{-1}) and the equation

$$\frac{\Delta S^{\circ}_{\text{exptl}}}{R} = 2x \ln x + (1 - 2x) \ln (0.5 - x) \qquad (1)$$

where x is the mole fraction of I and VI and $(0.5 - x)$ that of II and III. Then the proportions of I and VI will be about 36% and those of II and III about 14%. Thus the free-energy difference between I (or VI) and II (or III) is about 2.3 kJ mol^{-1} (0.55 kcal mol^{-1}).

The excess enthalpy of I and VI with respect to the unsubstituted twist conformations was assumed to amount to 2 kJ mol^{-1} (0.5 kcal mol^{-1}; see before) and hence that of II and III (if the twist forms do not differ in entropy) will be (2 + 2.3) = 4.3 kJ mol^{-1} (1.03 kcal mol^{-1}), also in close agreement with the preceding postulation.

Since

$$\Delta H = \Sigma x_i \Delta H_i$$

the total excess enthalpy of *r*-2-*tert*-butyl-2, *trans*-6-dimethyl-1,3-oxathiane will be $\Delta H^{\circ}_{\text{CT}}$ +2.64 kJ mol^{-1} ($\Delta H^{\circ}_{\text{CT}}$ +0.63 kcal mol^{-1}) over that of an unsubstituted chair form. The conformational enthalpy of an axial methyl group at position 2 in the 1,3-oxathiane ring has been determined (13.6 kJ mol^{-1} = 3.25 kcal mol^{-1}).[4a] Owing to the geminal substitution[2g,9] this interaction in *r*-2-*tert*-butyl-2,*cis*-6-dimethyl-1,3-oxathiane is likely to be slightly enhanced to, say, 14.6 kJ mol^{-1} (3.5 kcal mol^{-1}).

Now we are able to derive a value for $\Delta H^{\circ}_{\text{CT}}$ from the experimental enthalpy difference (13.24 kJ mol^{-1} = 3.16 kcal mol^{-1}) between the epimeric 1,3-oxathianes (Table I), since $\Delta H^{\circ}_{\text{exptl}} = [\Delta H^{\circ}_{\text{CT}} + 2.64\ (0.63)] - 14.6\ (3.50)$ and $\Delta H^{\circ}_{\text{CT}} = 13.24\ (3.16) - 2.64\ (0.63) + 14.6\ (3.50) = 25.2$ kJ mol^{-1} (6.0 kcal mol^{-1}). This estimate is not far from the gas-phase value, 22.5 kJ mol^{-1} (5.4 kcal mol^{-1}), based on appearance potential measurements.[5] Moreover, the latter value should in fact be revised upwards because of the double-buttressing effect in the reference chair form, 2,2,*cis*-4,6-dimethyl-1,3-oxathiane. In 2,2,*cis*-4,6-dimethyl-1,3-dioxane the magnitude of this effect is about 3.1 kJ mol^{-1} (0.74 kcal mol^{-1}).[2c,e,g] By comparing the corresponding interactions in 1,3-dioxanes[2b-e] and in 1,3-oxathianes[4,5] with each other the double-buttressing effect in 2,2,*cis*-4,6-dimethyl-1,3-oxathiane may be estimated at 2.5 kJ mol^{-1} (0.60 kcal mol^{-1}). Consequently, the corrected value of $\Delta H^{\circ}_{\text{CT}}$ (g) is about 25 kJ mol^{-1} (6.0 kcal mol^{-1}).

1,3-Oxathiane itself has six possible twist conformations but only two possible chairs.[10] If all the twists are of the same energy, $\Delta S^{\circ}_{\text{CT}}$ should be $R \ln 3$ or 9.13 J mol^{-1} °K^{-1} (2.18 cal mol^{-1} °K^{-1}) and, accordingly, $\Delta G^{\circ}_{\text{CT}}$ = 22.5 kJ mol^{-1} (5.4 kcal mol^{-1}). If any of the twist forms predominates, then $\Delta S^{\circ}_{\text{CT}}$ will be somewhat smaller and $\Delta G^{\circ}_{\text{CT}}$ somewhat higher. Thus we can estimate $\Delta G^{\circ}_{\text{CT}}$ to be 23 ± 2 kJ mol^{-1} (5.5 ± 0.5 kcal mol^{-1}) at 298°K.

It may be of some interest to compare chair–twist energy differences in cyclohexane, 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane, and this has been done in Table II. The parameters presented for the 1,3-dithiane ring in ref 3 are suitable for 2,5-disubstituted derivatives only.[3] Other 1,3-dithianes[11] have clearly greater $\Delta H^{\circ}_{\text{CT}}$ (16–20 kJ mol^{-1} or 4–5 kcal mol^{-1}) and $\Delta G^{\circ}_{\text{CT}}$ (10–14 kJ mol^{-1} or 2.4–3.4 kcal mol^{-1}).

Experimental Section

r-2-*tert*-Butyl-2,*cis*-6-dimethyl-1,3-oxathiane was prepared earlier.[12] The equilibration method and the analysis of the equilibrium mixtures have been described before.[4]

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Registry No.—*r*-2-*tert*-Butyl-2,*trans*-6-dimethyl-1,3-oxathiane, 51271-30-8; *r*-2-*tert*-butyl-2,*cis*-6-dimethyl-1,3-oxathiane, 51271-31-9.

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Rearrangements of α,β-Unsaturated α′-Halocyclobutanones

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The base-catalyzed ring contraction of α-halocyclobutanones has been the subject of considerable study in recent years.[1] We have recently synthesized some α,β-unsaturated α′-halocyclobutanones[2] and now reveal the unexpected results obtained upon base treatment of such compounds.

The treatment of 10-chloro-10-methylbicyclo[7.2.0]undec-1-en-11-one (I) with sodium methoxide in methanol resulted in allylic substitution rather than ring contraction to produce the 3-methoxy ketone II. The substitution