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RING INVERSION IN TRIMETHYLENE SULFATES

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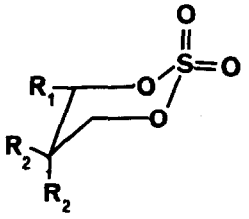
A recent publication[1] cites an ultrasonic relaxation experiment on 4-methyltrimethylene sulfate (1a) which is interpreted in terms of a chair/chair ring inversion with a barrier of $\Delta H^{\ddagger}$= 6.2 kcal/mole (more stable ⟶ less stable).[2] Consideration of this molecule seemed to offer no explanation for the marked difference between this value and that of 10.3 kcal/mole for cyclohexane.[3] In order to verify the published result, we prepared the related 5,5-dimethyltrimethylene sulfate (1b) and recorded its low-temperature n.m.r. spectrum. The barrier to chair/chair inversion of 1b is 8.1 ± 0.2 kcal/mole based on the coalescence of the AB methylene quartet (Tc= -107°C; J_{AB}= 10.5 ± 0.1 Hz.; $\Delta\nu_{AB}$= 24.5 Hz.) or 8.4 ± 0.2 kcal/mole based on the coalescence of the methyl singlets (Tc= -109°C; $\Delta\nu$= 22.0 ± 0.1 Hz.).[4] For trimethylene sulfate itself, preliminary experiments have indicated that the barrier is of a similar magnitude, indicating that the steric interactions in 1b do not affect the barrier significantly.

For a chair/chair interconversion, the barrier in 4-methyltrimethylene sulfate (1a) would be expected to be at least as great as that for 1b. Since it is known that the ultrasonic relaxation technique cannot, by itself, lead to any identification of the species involved in a conformational equilibrium[5] it seems likely that the value of 6.2 kcal/mole is a measure of the conformational barrier between a chair and an energetically low-lying non-chair form. A similar situation has appeared in a substituted 1,3-dioxane

where acoustical measurements[6] give $\Delta H^{\ddagger} = 5.0$ kcal/mole, whereas n.m.r. experiments give a value of 8.4 kcal/mole.[7] This apparent conflict has been resolved by assigning the lower barrier to a chair/non-chair change.[6]

The implications of these results for the conformational analysis of trimethylene sulfites will be the subject of a future publication.



1a $R_1 = CH_3$ $R_2 = H$

1b $R_1 = H$ $R_2 = CH_3$

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