Tetrahedron Letters No. 31, pp. 2937-2940, 1971. Pergamon Press. Printed in Great Britain.

THE BARRIER TO RING REVERSAL IN 5,5-DIMETHYL-1,3,2-DIOXATHIANE

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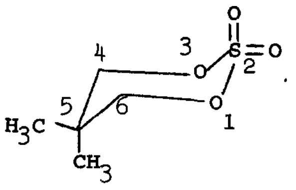
It has been found that successive introduction of adjacent sulfur atoms in place of methylene groups in thiane[1] raises the barriers to ring reversal[2,3,4] appreciably. This is in agreement with the measured values[5,6] and also with the theoretical predictions of Wolfe and co-workers,[7] which state that electron pair-electron pair, electron pair-polar bond or polar bond-polar bond interactions cause a significant increase in rotation-inversion barriers.

Efforts to observe the conformational isomers of various trimethylene sulfites[8] and 1,2-oxathiane 2-oxide[9] by variable temperature n.m.r. spectrometry have been unsuccessful. These results rule out conformational equilibria across a barrier of magnitude comparable to that anticipated for chair-chair ring reversal.

Recently, it has been reported from this laboratory that the barrier to chair-chair interconversion in 5,5-dimethyltrimethylene sulfate (1)was 8.1-8.4 kcal/mole.[10] This value is approximately 2.0 kcal/mole less than that of cyclohexane[11] but apparently higher than a cyclic sulfate barrier measured by ultrasonic absorption and attributed to ring reversal.[12] This n.m.r. result presumably arises from a balancing of several factors, including electron pair-polar bond[7] interactions across the S-O bonds and reduced rotational barriers about the C-O bonds.



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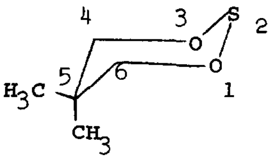

2

In an attempt to gain more information about the influence of vicinal electron pair interactions on the barrier height, we examined 5,5-dimethyl-1,3,2-dioxathiane (2). In this communication, we report the low temperature n.m.r. behaviour[13] of compound 2. To our knowledge, this system has not been studied before.

This compound was prepared following the procedure of Thompson[14] and obtained as a mixture of 5,5-dimethyl-1,3,2-dioxathiane and 5,5-dimethyltrimethylene sulfite by distillation. These could be separated by gas-liquid chromatrography (g.l.c.) using a column (5 1/2' x 1/4") packed with 10% diethylene glycol succinate (LAC 728) on Chrom W. The desired sulfoxylate ester 2 had the lower retention time.

The elemental analysis agreed with the formula for compound 2.[15] Further confirmation of the molecular weight was obtained by mass spectrum[16] which gave m/e 134 as parent. The elemental composition, deduced by measuring the relative intensities of M+1 and M+2 with respect to the molecular ion, agreed with the combustion result. No evidence for the corresponding sulfite, a possible contaminant, could be detected in the mass spectrum.

At room temperature, the proton resonance spectrum showed two singlets at $\tau 6.0$ and $\tau 9.0$ indicating that the ring was interconverting rapidly at this temperature. By cooling, the following results were obtained.

The barrier ($\Delta G^{\ddagger}$) to chair-chair reversal in 2 has been found to be 12.6 ± 0.2 kcal/mole based on the coalescence of the methyl signals ($T_c = -20^{\circ}C$; $\Delta\nu = 29.3 \pm 0.1$ Hz) and 12.3 ± 0.2 kcal/mole obtained from the coalescence of the methylene quartet ($T_c = -26^{\circ}C$; $J_{AB} = 10.7 \pm 0.1$ Hz; $\Delta\nu_{AB} = 13.7 \pm 0.1$ Hz).[17]

A preliminary investigation of the parent 1,3,2-dioxathiane showed that the barrier in this system may be slightly lower. We are currently involved in labelling this compound with deuterium in order to determine the accurate value.

The present result is consistent with a sufficiently high S-O rotational barrier to counterbalance the known[18] lower C-O barrier (2.7 kcal/mole) and produce a ring reversal barrier higher than cyclohexane.

Further consideration of the meaning of this result will be included in a more complete report on conformational properties of 1,3,2-dioxathianes to be published elsewhere.

Acknowledgement: We thank the National Research Council of Canada for financial support, and Dr. M. H. Miskow and Mr. D. Hill for technical assistance.

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13. N m.r. spectra were recorded in methylene chloride-d_2 solution on JEOL C-60 HL spectrometer with tetramethylsilane as internal reference.

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15. The compound was isolated as colorless liquid by g.l.c. Reinjection of a small quantity, under similar conditions, showed some decomposition. However, the i.r., n.m.r. and mass spectra, of the liquid isolated by g.l.c., were in complete agreement with the structure.

16. The mass spectrum was done by Morgan-Schaffer Corporation, Montreal, Canada.

17. See Ref. 5, p. 113, 122.

18. J. P. Lowe, "Barriers to Internal Rotation about Single Bonds, " A. Streitwieser, Jr., and R. W. Taft, Ed., "Progress in Physical Organic Chemistry," Vol. 6, Interscience, New York, 1968, p. 44. No experimental determination of the S-O torsional barrier has been made but there is considerable evidence that torsional barriers are high whenever vicinal electron pairs are present. See Table in this reference and also see reference 7.