

STEREOCHEMISTRY OF DICOORDINATED OXYGEN. I. NMR STUDIES OF
DOUBLY ORTHO-BRIDGED DIPHENYL ETHERS AND THE POSSIBILITY OF OXYGEN INVERSION

Arnold J. Gordon and John P. Gallagher

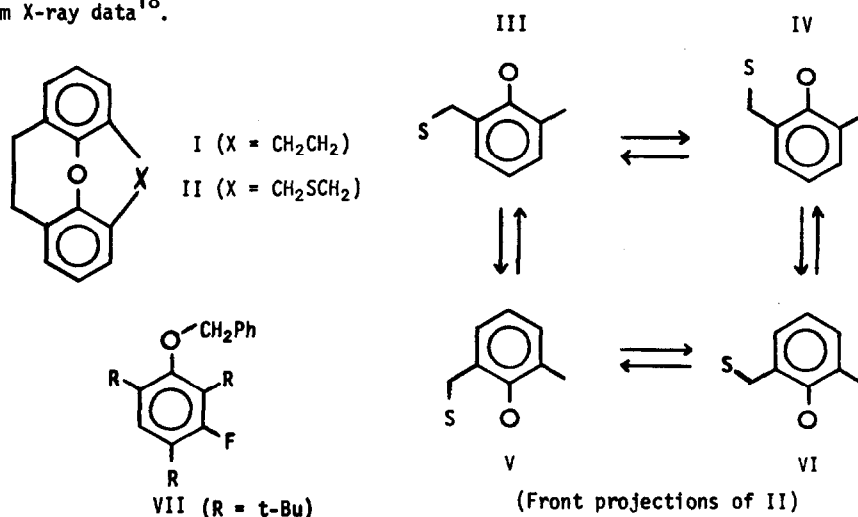
Department of Chemistry, The Catholic University of America, Washington, D. C. 20017

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It was suggested in 1933 that suitably o-substituted diaryl ethers might be capable of resolution into enantiomers¹. Since then, several studies have been made on crowded aryl ether conformations using ir, uv and dipole moment techniques²; unsuccessful attempts to separate ether diastereomers have also been made³. Miller pointed out⁴ that for acyclic, divalent oxygen, rotation and inversion processes lead to identical conformations and that no knowledge exists concerning the involvement of inversion. This "two-dimensional" inversion process (as contrasted to that for amines) would have ideally, a linear transition state^{5,6}; it is operationally related to the in-plane inversion mechanism for syn-anti isomerism in imines and related nitrogen compounds⁷.

In an initial attempt to gauge the possibility of stereoelectronic inversion at ether oxygen, we have examined the highly rigid ethers I and II. Compounds I (8,16-oxido[2.2]metacyclophane)⁹ and II (9,17-oxido-2-thia[3.2]metacyclophane)¹⁰ are constrained into cis (butterfly) conformations, unlike the trans (ladder) geometry of ordinary metacyclophanes¹¹, but like that of an 8,16-methano[2.2]metacyclophane¹². The nmr spectrum of II in chlorobenzene at r.t. (Varian A-60, internal TMS; sealed under N₂) shows an AB quartet (H-1 and H-3; $\Delta\nu_{AB}=48.4$ Hz, $J=14.5$) and an AA'BB' multiplet (H-10 and H-11; centered at $\nu \sim 170$ Hz). Both absorptions represent an average for two conformations of the sulfur bridge (III \rightleftharpoons IV or V \rightleftharpoons VI). Sulfur heterocycles have already been shown to have low energy barriers to ring inversion^{13,14}. Above 80° the spectrum gradually changes until both the AB and AA'BB' portions coalesce at 130°; at 175° the entire benzyl proton region consists of two sharp singlets (1/2 width 1.5 Hz) in the ratio 1/1 (H-1 and H-3, δ 3.93; H-10 and H-11, δ 3.03). This behaviour is completely reproducible over several temperature cycles and II was recovered unchanged (glc, tlc, ir).

To insure that bond breaking formation of short lived radicals is not involved, a sample of II was heated in chlorobenzene at 200° (sealed tube; N₂) for an hour in the presence of excess 2,4,6-tri-*t*-butylphenol; no change was detected. From the approximation formula¹⁶, $k_c = 133 \text{ sec}^{-1}$ whereby $\Delta G_c^\ddagger = 20.0 \text{ k.cal./mole}$. In contrast to II, compound I displayed virtually no change in the AA'BB' spectrum up to ~190°; the difference in behaviour is undoubtedly due to the more restrictive [2.2] bridges and to the actual space limitations for oxygen movement¹⁷, as determined from X-ray data¹⁸.



The restraining bridges in I and II clearly prohibit normal rotation about the O-phenyl carbon bonds. The nmr observations are thus consistent with both (or a combination of) an inversion process for oxygen and an unusual libration involving ring inversion, presumably within the 8-ring containing sulfur ($\text{III} \rightleftharpoons \text{V}$ and $\text{IV} \rightleftharpoons \text{VI}$). The mechanism is clearly different from restricted rotations observed with acyclic diaryl ethers¹⁹ and crowded benzyl phenyl ethers (VII)^{10, 17}; for these systems, T_c values are less than ~50° and ΔG_c^\ddagger values are generally <18 k.cal./mole¹⁹. Studies are in progress to make a finer distinction between a pure inversion and alternative mechanisms²⁰.

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References and Footnotes

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14. Preliminary low temperature nmr studies of II show expected broadening of the AB system to two AB spectra. Dipole moment measurements are also in progress to establish the equilibrium concentrations of IV and III; based on steric considerations (models) and the operation of a "rabbit-ear effect"¹⁵, the endo-sulfur conformation (III) is expected to be the more stable.
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20. The belief that "fast configurational inversion at the oxygen atom" occurs in an N-Methoxyamine (footnote 17 in J. E. Anderson, D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 6371 (1969)) was incorrectly based on reference to Lambert's oxonium ion inversion studies⁶. Preliminary LCAO-MO-SCF calculations on simple oxygen compounds indicate for water, using a basis set of 8s3p on O and 3s on H, a barrier for inversion in excess of 34 k.cal./mole (A. J. Gordon and W. A. Sanders, unpublished results).