

binations ($2a_1 + a_2 + 3e$) available for direct metal-metal interactions (as well as for π bonding with the S ligands) develop into four *bonding* ($2a_1 + e$) and five *antibonding* ($a_2 + 2e$) delocalized trimetal orbitals (relative to the energies of the isolated AO's of each metal atom). Furthermore, in order to account for the diamagnetism of $[\text{Mo}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+$, it is presumed from orbital overlap considerations that the six electrons available for direct Mo-Mo interactions occupy $a_1 + e$ bonding combinations, with the remaining a_1 trimetal bonding combination being empty. The application of this same MO scheme to the isostructural, diamagnetic $\text{Mn}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{NO})_4$ molecule, for which each Mn conforms to the noble-gas rule, indicates that the 12 electrons available for placement into the 9 trimetal orbitals inhabit, in addition to the a_1 and e bonding levels (filled in $[\text{Mo}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+$), the other a_1 bonding level along with a doubly degenerate antibonding e one. Complete occupation of these least two levels would tend to cancel each other in terms of metal-metal interactions, and therefore from a localized valence-bond viewpoint both the $[\text{Mo}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+$ cation and the $\text{Mn}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{NO})_4$ molecule possess electron-pair metal-metal bonds.

This MO model, which focuses primary attention on the metal cluster bonding,¹³ predicts (1) the possibility of reduction of the $[\text{Mo}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+$ cation; (2) the feasibility of attempting to prepare the unknown molecule (or cations) of $\text{M}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_4$ (where $\text{M} = \text{Ru}, \text{Os}$); (3) the possibility of oxidation of $\text{Mn}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{NO})_4$. In fact, a cyclic voltammogram of the $[\text{Mo}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+[\text{Sn}(\text{CH}_3)_3\text{Cl}_2]^-$ salt in CH_2Cl_2 gives a one-electron reduction wave at -0.55 V (*vs.* sce). Further studies are being carried out to substantiate these predictions, and full details of our communication presented here will be reported upon completion of this work.

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(13) The qualitative symmetry arguments and resulting predictions are assumed to be valid despite extensive mixing, which no doubt occurs among metal-ligand and trimetal symmetry orbitals belonging to a given representation.

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Ring Inversion Barrier of 1,4-Dioxane

Sir:

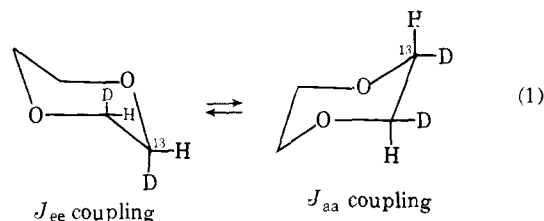
Whereas the nmr spectrum of cyclohexane¹ separates from a singlet into a multiplet at -65° , the 1,4-dioxane protons appear as a sharp singlet even at -160° with a width at half-height comparable to that of TMS.^{2,3}

(1) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Amer. Chem. Soc.*, **82**, 1256 (1960).

This anomalous behavior has three possible explanations. First, the chair-to-chair inversion barrier may be lower than $\sim 5 \text{ kcal/mol}$ (ΔG^\ddagger). Second, dioxane may exist predominantly in a boat form which pseudorotates with a low energy barrier. Third, a coincidence of the axial and equatorial resonances may exist at low temperatures.

In examining the proton spectrum of 1,4-dioxane, it was noted that the ^{13}C side bands appear as multiplets. The multiplet structure of the side band has been the textbook example^{4,5} of chemical shift nonequivalence induced by coupling with the natural-abundance ^{13}C nucleus. The multiplet observed is a time-average spectrum resulting from rapidly interconverting forms of dioxane.⁶ It was therefore hypothesized that at a temperature sufficiently low to cause the inversion process to be slow on the nmr time scale, significant changes would occur in the coupling in the ^{13}C side bands. With this idea in mind, the ^{13}C side-band proton spectrum of dioxane was investigated at low temperatures. A change is observed at approximately -90° . However, the peaks are broad and overlap and hence are difficult to analyze.

In order to simplify the ^{13}C side bands, a specifically deuterated dioxane was synthesized. For this purpose 2,3,5,6-dioxane- d_4 , in which the relationship of the deuterium atoms of the $-\text{OCHDCHDO}-$ moiety is trans, was prepared.⁷ This isomer was selected because at low temperature in the ^{13}C side bands, the individual J_{ee} and J_{aa} couplings are expected to be observed (eq 1),



and the side band is expected to consist of a pair of doublets. At room temperature, each side band is expected to exist as a doublet with $J = 1/2(J_{aa} + J_{ee})$.

Spectra of the trans-trans compound were obtained in a solvent mixture of 10% TMS, 37% CH_2Cl_2 , 37% $\text{CH}_2=\text{CHCl}$, and 16% dioxane- d_4 (volume %). At room temperature, the expected spectrum for the upfield side band consisting of a doublet of 6.5 Hz was observed. (The low-field side band was not investigated owing to the nearness to side bands of the solvents.) At -103° , the spectrum of the upfield side band consisted of a doublet ($J_{aa} = 11.7 \text{ Hz}$) and an unresolved doublet ($J_{ee} = \text{ca. } 1 \text{ Hz}$) (Figure 1). However, the J_{ee} doublet is not centered within the J_{aa} doublet as was expected. The reason for this lack of symmetry is explained below.

(2) A. J. Berlin, Ph.D. Thesis, University of California, Berkeley, 1963.

(3) (a) C. H. Bushweller, Ph.D. Thesis, University of California, Berkeley, 1966; (b) B. Pedersen and J. Schaug, *Acta Chem. Scand.*, **22**, 1705 (1968).

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 163.

(5) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 147.

(6) J. B. Lambert, *J. Amer. Chem. Soc.*, **89**, 1836 (1967).

(7) The synthesis of this compound will appear in a forthcoming paper.

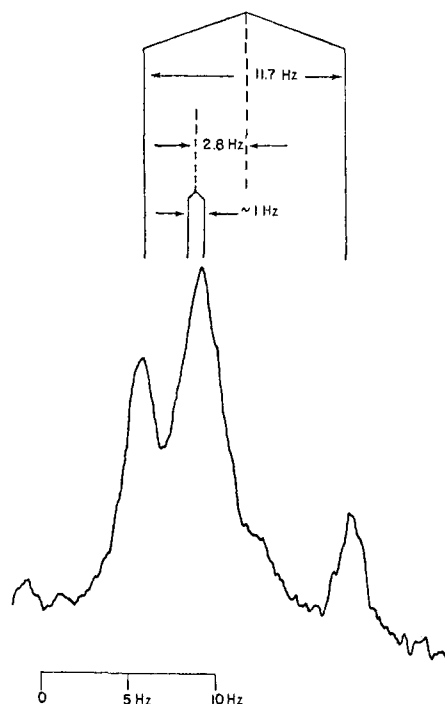


Figure 1. Upfield ^{13}C side band of *trans*-2,3-*trans*-5,6-dioxane- d_4 at -103° (100 MHz, deuterium decoupled, computer enhanced, ten scans), showing the J_{aa} coupling of 11.7 Hz, and the unresolved J_{ee} coupling of ~ 1 Hz (based on computer simulation).

Surprisingly, and to our delight, at low temperature the center proton resonance had separated into two peaks. This could only arise by the axial and equatorial protons on the carbons bearing deuterium having different chemical shifts, while in dioxane itself the resonances occur at (essentially) identical positions.

Further experiments indicated that in this solvent system at -104° , 1,4-dioxane- d_0 has a chemical shift of δ 3.67 while the two peaks of *trans*-2,3-*trans*-5,6-dioxane- d_4 have been shifted upfield to δ 3.66 and 3.63. (At room temperature, the relative shifts are δ 3.61 for dioxane- d_0 and δ 3.58 for the fast-exchange spectrum of the deuterated 1,4-dioxane.) By comparison with the unsymmetrical spectrum of the ^{13}C side band (the unresolved J_{ee} doublet is shifted downfield from the center of the J_{aa} doublet; see Figure 1), and assuming that $J_{^{13}\text{C}-\text{H}_{ax}} = J_{^{13}\text{C}-\text{H}_{eq}}$, the resonance at δ 3.66 was assigned to the equatorial protons and the resonance at δ 3.63 to the axial protons.

It now appeared that the inversion barrier could most simply be obtained by observing the changes in the spectrum of dioxane- d_7 with change in temperature. For this purpose dioxane- d_8 was prepared and mass spectral analysis showed the presence of 7% dioxane- d_7 . This compound gives a sharp singlet at room temperature (deuterium decoupled), and at -104° it appears as two sharp singlets (deuterium decoupled) with a separation of 3.34 Hz (Figure 2).

By observing the pmr spectrum at various temperatures and subjecting the data to computer analysis,³ a barrier to inversion of $\Delta G^\ddagger = 9.70$ kcal/mol at -93.6° is obtained. This barrier assumes a twist form as intermediate and represents the chair-twist barrier (eq 2).

(8) G. Binsch and D. A. Kleier, Program DNMR 3 obtained from Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind. 47401.

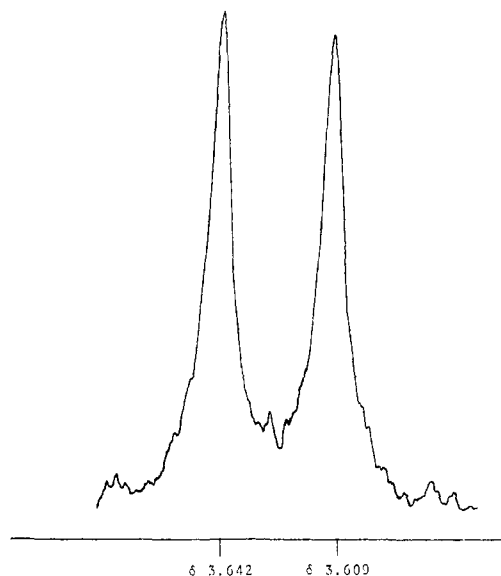
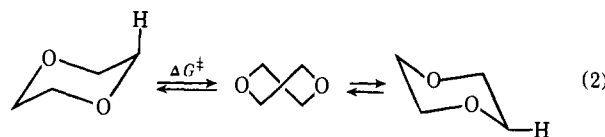


Figure 2. Dioxane- d_7 at -107° (100 MHz, deuterium decoupled, TMS lock), showing the separate resonances of the equatorial (δ 3.642) and axial (δ 3.609) protons.

An effort is underway to determine ΔH^\ddagger for this process. However, it is likely that the major factor contributing to ΔS^\ddagger is the degeneracy of the reaction as is the case for



cyclohexane. A recent calculation of the chair-twist barrier of dioxane yielded a value of $\Delta G^\ddagger = 10.1$ kcal/mol.⁹

The magnitudes of the observed coupling constants in the ^{13}C side bands provide compelling evidence that dioxane exists in the chair form. The observed normal barrier for dioxane also supports this belief. X-Ray analysis of crystalline dioxane has previously demonstrated that it exists as the chair form in the solid state.¹⁰

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(9) H. M. Pickett and H. L. Strauss, *J. Amer. Chem. Soc.*, **92**, 7281 (1970).

(10) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

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Importance of $^1n, \pi^*$ States in N-Heterocycles. Internal Conversion, Intersystem Crossing, and Isomerization in Azastilbenes

Sir:

Previously, we reported photoaddition and photoreduction reactions of acridine and 1,2-bispyridylethylenes originating from low-lying $^1n, \pi^*$ states.^{1,2} We now report results which more clearly delineate the

(1) D. G. Whitten and Y. J. Lee, *J. Amer. Chem. Soc.*, **92**, 415 (1970).

(2) D. G. Whitten and Y. J. Lee, *ibid.*, **93**, 961 (1971).