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# THE ELECTRONIC NATURE OF TRIMETHYLENEMETHANE

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Two recent communications describe the production of trimethylenemethane from 4-methylene-1-pyrazoline. Dowd (2) has decomposed the pyrazoline photolytically and observed the esr spectrum of the ground state triplet. Crawford and Cameron (3) have obtained methylenecyclopropane from the thermal decomposition of the pyrazoline and invoke trimethylenemethane as an intermediate to account for the observed deuterium scrambling. Theoretical considerations are presented here which suggest that the two methods of production lead to different electronic states of trimethylenemethane which exhibit divergent chemical behavior.

Highly symmetrical systems of the type considered here allow the rigorous application of group theoretic considerations to the construction of correlation diagrams (4, 5). Depending on whether the pyrazoline is transformed to trimethylenemethane in a conrotatory or disrotatory mode, a $C_2$ axis or plane of symmetry is applicable. In either case the ground state of the pyrazoline must be symmetric and correlate with the lowest state of the same symmetry in trimethylenemethane. The allowed $n \rightarrow \pi^*_{N=N}$ transition gives rise to a state which is correlated with the lowest antisymmetric state of trimethylenemethane in a conrotatory mode and with a symmetric state in a disrotatory reaction.

The symmetry of the molecular orbitals of trimethylenemethane enables the symmetry classification of the electronic states in the conrotatory and disrotatory modes. The ordering of their energies is accomplished by a simple Pariser-Parr-Pople (6,7) calculation, and correlations can then be established using the rule that states of the same symmetry and spin multiplicity do not cross. The resulting diagrams are shown in Figures I and II. The states of trimethylenemethane are labeled with their classification in the full symmetry group appropriate to the molecular geometry.

**Inspection of the diagrams shows that** the thermal decomposition of the pyrazoline

FIG. 1

Correlation Diagram for Conrotatory Reactions

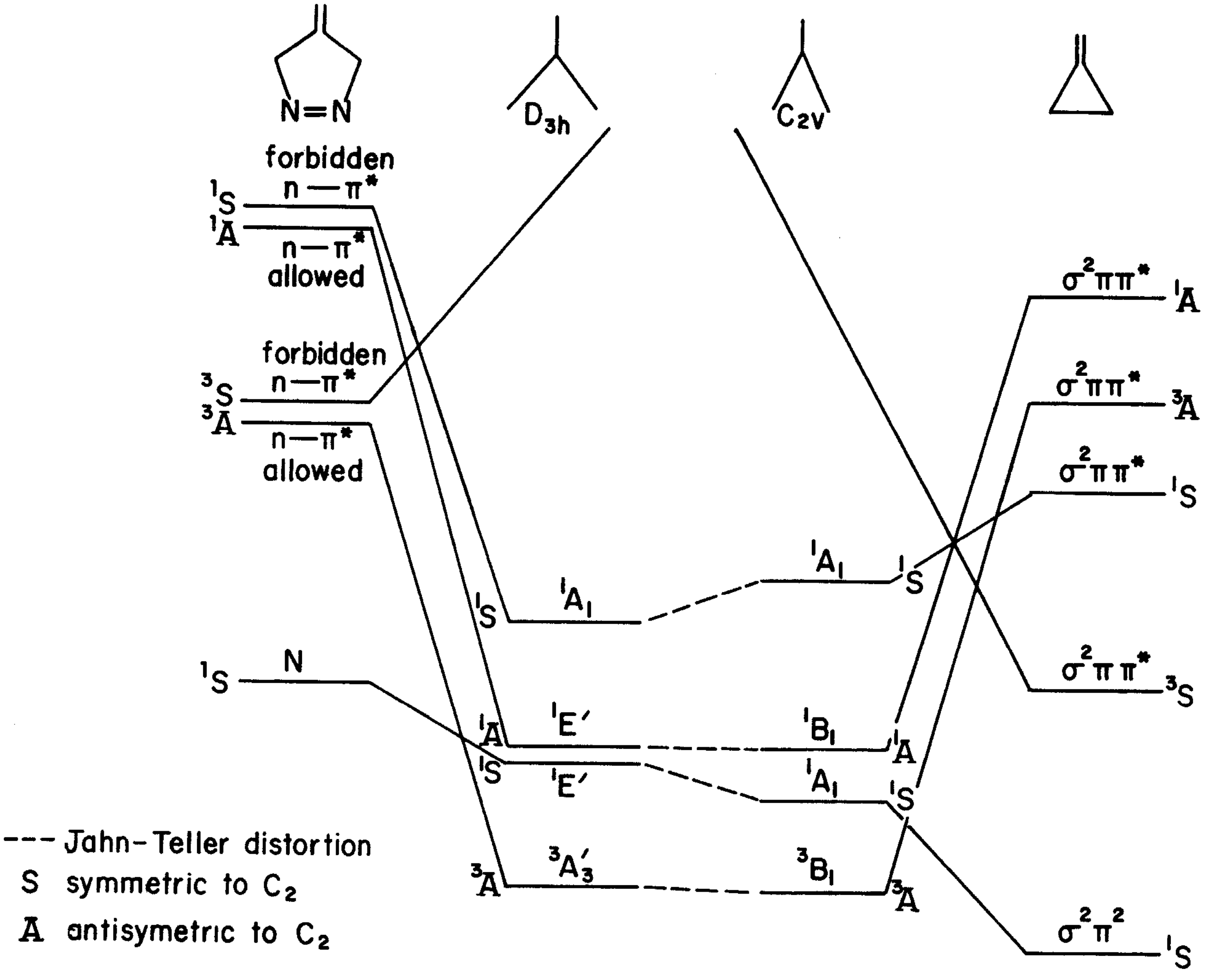
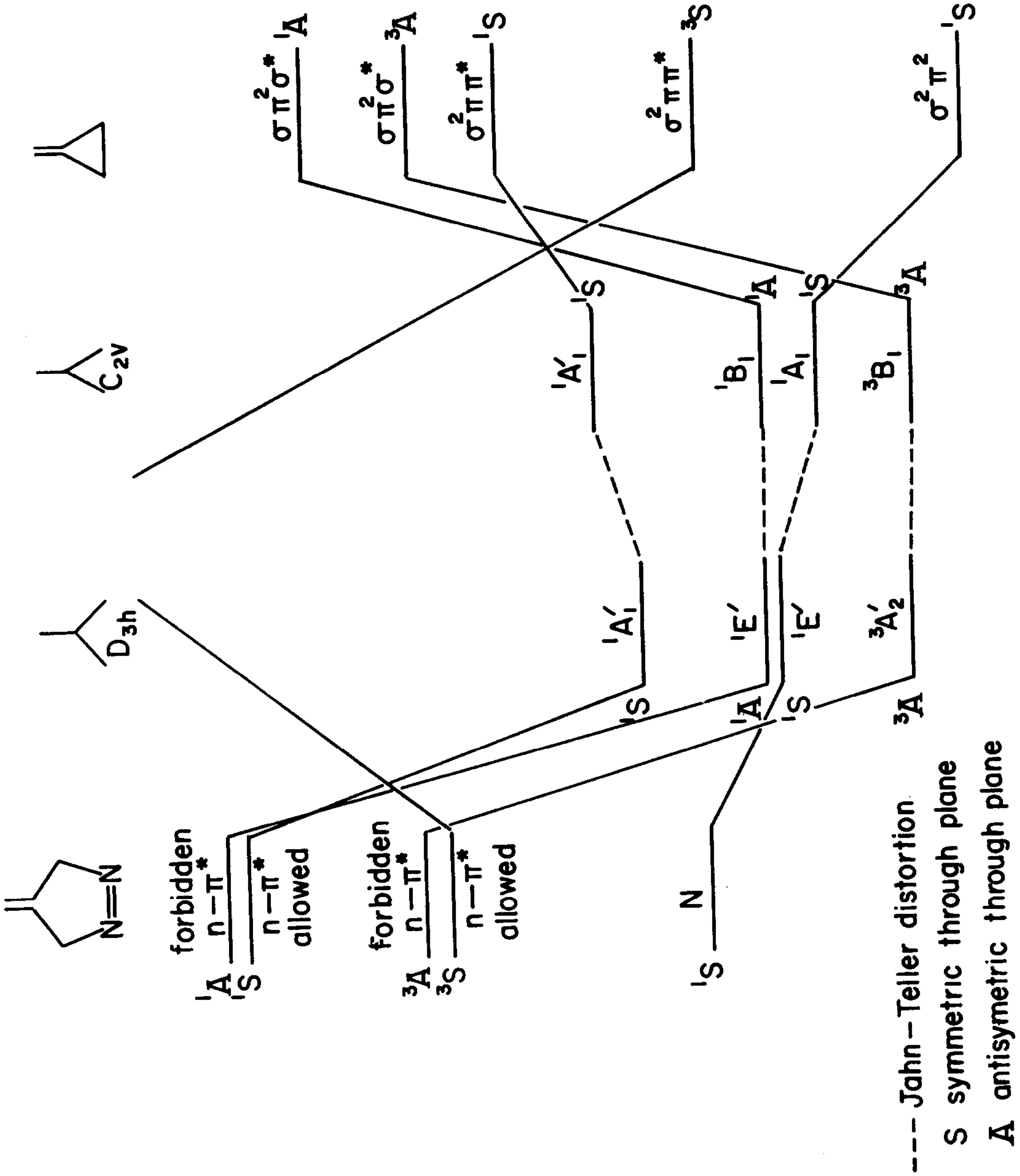


FIG. 2

Correlation Diagram for Disrotatory Reactions



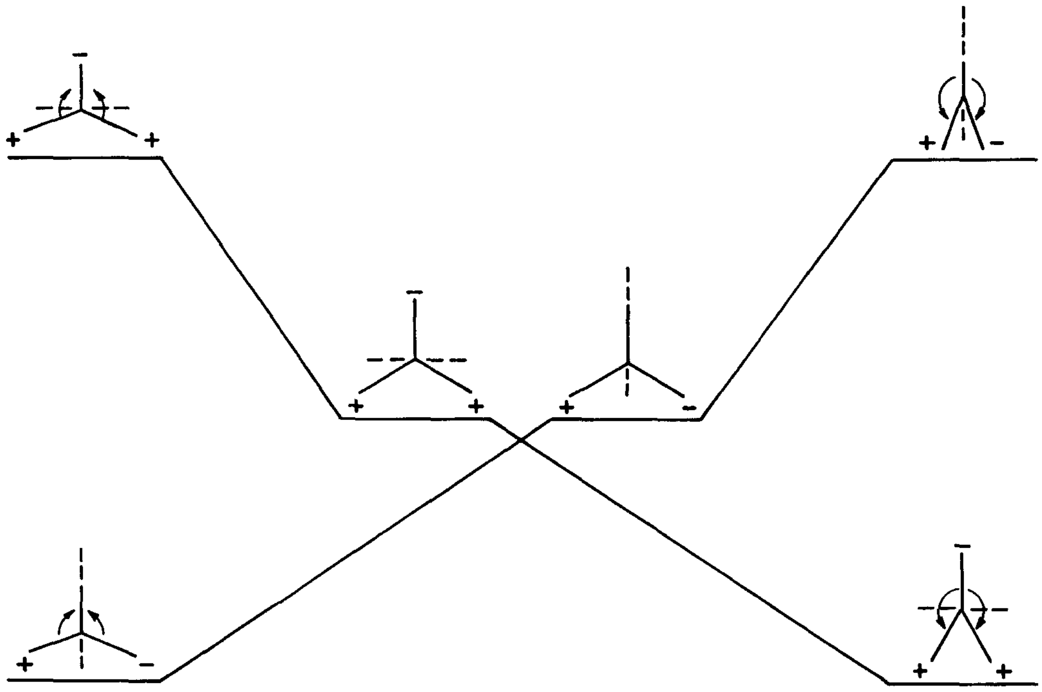
in a concerted fashion should not yield the triplet ground state directly; however, it is possible that n→π* $_{N=N}$ excitation followed by intersystem crossing and decomposition could produce this species. Therefore, it is not surprising that the photochemical route led to the observation of triplet trimethylenemethane. Of course, thermally produced singlet trimethylenemethane might undergo intersystem crossing to the ground state triplet; however, the possibility must be considered that competitive with crossing to the ground state is closure of the trimethylenemethane to methylenecyclopropane. The correlation diagrams show that this latter process can proceed facilely in either a conrotatory or disrotatory fashion from the lowest singlet. Moreover, the $^1E'$ state is subject, according to the Jahn-Teller theorem (8), to a distortion from $D_{3h}$ to $C_{2v}$ symmetry. Such a distortion to lower symmetry lifts the degeneracy of the $^1E'$ states by lowering the energy of one of the non-bonding MO's and raising that of the other. One allowed distortion is such that two of the terminal carbon atoms move closer together so that the electrons tend to occupy the MO where bonding between these atoms can occur, as shown in Figure III. This distortion, moving two of the carbon atoms together while developing a bond between them, orients the molecule favorably for disrotatory closure to methylenecyclopropane. This probably is the situation which obtains in the thermal decomposition of the pyrazoline--a singlet trimethylenemethane is produced which quickly closes to methylenecyclopropane. In circumstances where excess vibrational energy can be efficiently lost or partitioned, the closure may be so rapid that the methylene groups never become equivalent.

On the other hand, the triplet can only close to an excited state of methylenecyclopropane; and it is therefore predicted that little or none of this cyclic compound should be observed in a reaction yielding only the triplet species. Inversely, the production of methylenecyclopropane in large quantities rules out the intermediacy of the triplet trimethylenemethane. The fact that the pyrazoline was "quantitatively converted" (3) to methylenecyclopropane in the thermal decomposition supports the above theoretical conclusion that the reaction is unlikely to yield triplet trimethylenemethane.

Inspection of the correlation diagrams also leads to interesting conclusions regarding the chemistry of methylenecyclopropane. One predicts that a photosensitized triplet reaction should not lead to ring opening unless the proximity of the sensitizer invalidates arguments based on symmetry considerations or the triplet undergoes demotion back to a vibrationally "hot" ground state from which opening occurs.

FIG. 3

Effect of Jahn-Teller Distortion on Non-Bonding MO's of Trimethylenemethane



In contrast, thermolysis should be capable of yielding a singlet trimethylenemethane intermediate, a conclusion supported by the known behavior of methylenecyclopropane (9,10).

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