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CORRELATION DIAGRAMS FOR THE CONCERTED π-σ BOND TRANSFORMATION REACTIONS [1]

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Woodward and Hoffmann have offered a correlation diagram for the disrotatory conversion of butadiene to cyclobutene as shown by dotted lines in Fig. 1.[2] We now wish to propose a new correlation diagram for this reaction as shown by solid lines in Fig. 1. This correlation diagram appears to violate the quantum mechanical non-crossing rule. However, a strict mathematical proof for this rule has been given for diatomic molecules in which only one parameter (interatomic distance) can be varied.[3] In connection with this, Teller has suggested[4] that for the case of polyatomic molecules where, in general, more than one parameter are necessary to describe the reaction process, we can not exclude the possibility of the crossing of energy surfaces only because their electronic states are identical in symmetry properties.

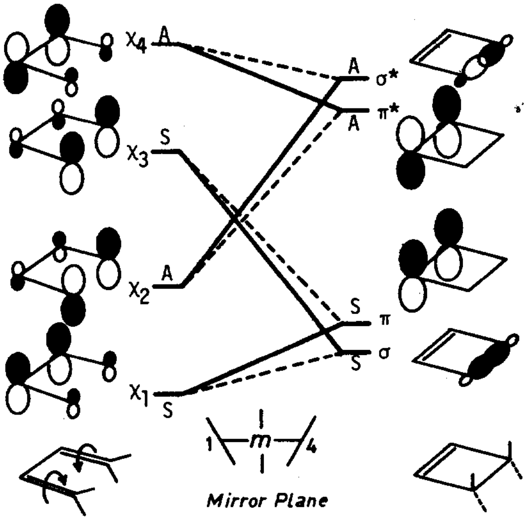


Fig. 1: Correlation diagram for the disrotatory conversion of butadiene to cyclobutene

In the disrotatory process in question, it is evident that we need at least two parameters to describe the reaction. For example, they are the interatomic distance (r) between C_1 and C_4, or the angle (ϕ) directly related to the ring closure, and the angle (θ) of the rotation of the p orbitals on C_1 and C_4 as shown in Fig. 2.

On the other hand, from Fig. 1, it is possible to say that the transfor-

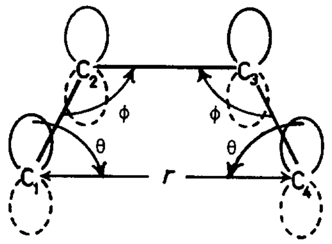


Fig. 2: The reaction parameters to describe the disrotatory conversion of butadiene to cyclobutene

mation of χ_1 orbital of butadiene to π orbital of cyclobutene is an interchange between π orbital and π orbital, whereas the transformation of χ_3 orbital of butadiene to σ orbital of cyclobutene is a change of π orbital to σ orbital. Practically, there is no energy interaction between the π orbitals and the σ orbitals of cyclobutene. In other words, they are orthogonal each other. So, it is not an unreasonable assumption that the above mentioned two transformation are orthogonal each other concerning to the reaction coordinate, and the crossing of the correlation lines may be allowed.

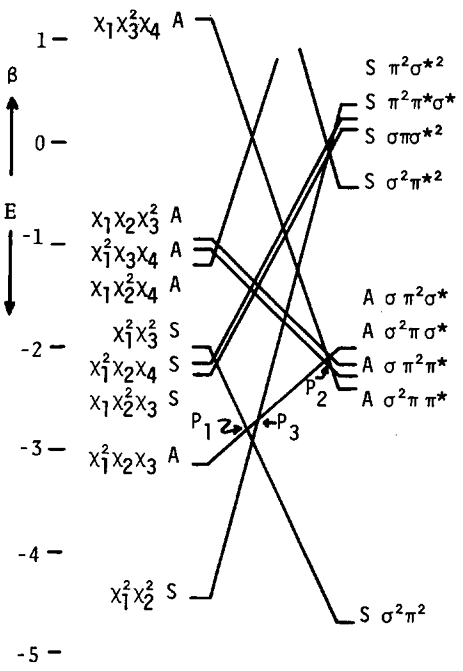


Fig. 3: Electronic state diagram for the disrotatory conversion of butadiene to cyclobutene

An electronic state diagram based on Fig. 1 for this reaction is shown in Fig. 3. This suggests that the reaction paths are not necessarily the same for the photochemical cyclization of butadiene to cyclobutene and for the reverse reaction, whereas the original state diagram proposed by Longuet-Higgins and Abrahamson[5] suggests the same reaction path for the cyclization and for the reverse reaction. For example, from Fig. 3, we can elucidate a probable reaction path for this reaction as follows: for photochemical cyclization of butadiene to cyclobutene; $\chi_1^2\chi_2^2 \xrightarrow{h\nu} \chi_1^2\chi_2\chi_3 \rightarrow P_1 \rightarrow \chi_1^2\chi_3^2 \rightarrow \sigma^2\pi^2$, for photochemical ring-opening of cyclobutene to butadiene; $\sigma^2\pi^2 \xrightarrow{h\nu} \sigma^2\pi\pi^* \rightarrow P_2 \rightarrow \sigma\pi^2\sigma^* \rightarrow P_3 \rightarrow \pi^2\sigma^{*2} \rightarrow \chi_1^2\chi_2^2$. It is worth-while to point out that both our state diagram and the above mentioned reaction paths have rather good similarities to those calculated by van der Lugt and Oosterhoff,[6] even though they have not questioned the use of the non-crossing rule.

In the same sense, correlation diagrams for disrotatory and conrotatory conversion of hexatriene to cyclohexadiene are shown in Fig. 4, where approximate energy levels are shown by the simple Hückel calculations. In such correlation diagrams, in general, the π orbitals of starting polyenes which should correlate to the σ orbitals of cyclic olefines are the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) with identical symmetry, having the highest electronic density at the terminal carbon atoms. Futher, when the actual Hückel molecular orbitals are drawn for each levels of the orbitals, it is obvious that the "shape" or "phase" of each π orbitals of the reactant, other than the HOMO or LUMO, is conserved in the correlated orbital of the product with a minimum deformation. Thus, we can correlate the orbitals of the reactant and product states, including the transition states along the reaction path, on the basis of highest overlap. At this point of view, it can be said that our correlation diagrams are an alternative application of Goddard's orbital phase continuity principle, or the principle of phase conservation,[7] for Hartree-Fock type or molecular orbital wave functions.

The correlation diagram for the conrotatory conversion in Fig. 4 also suggests that the reaction paths for the photocyclization and the reverse reaction are not same. This suggestion is again in agreement with both the experimental observations and a theoretical explanation for the photochemical transformation between previtamin D, lumisterol and ergosterol.[6, 8]

Finally, our new correlation diagram for the Diels-Alder reaction is shown by solid lines in Fig. 5. It is worth-while

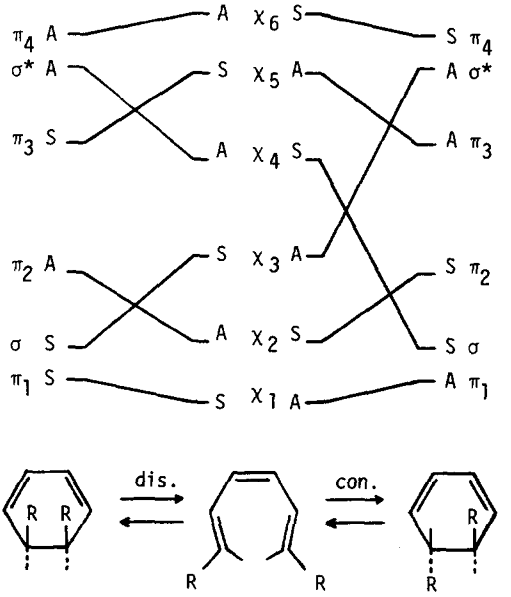


Fig. 4: Correlation diagrams for the disrotatory and conrotatory conversion of hexatrienes to cyclohexadienes

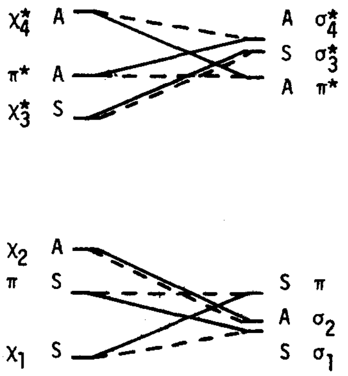
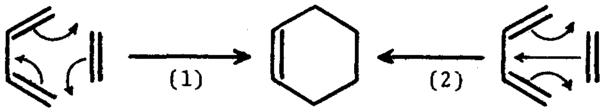


Fig. 5: Correlation diagram for the Diels-Alder reaction of butadiene with ethylene

to point out that our correlation diagram is also well-matched to the classical electronic formula (1) for this reaction, whereas, the Woodward-Hoffmann correlation diagram (dotted lines in Fig. 5) corresponds to some unfamiliar electronic formula (2).



Although, the latter formula (2) can be obtained by assuming an aromatic 6π transition state,[9] the actual Diels-Alder reactions are generally thought to proceed *via* parallel transition state rather than co-planar transition state. Therefore, at this point of view, our correlation diagram seems to represent more actual features of the reaction process.

In a similar manner, it is possible to draw much more reasonable correlation diagrams for wide variety of π-σ bond transformation reactions, including the sigmatropic reactions, and some of them will be presented in a later paper.

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