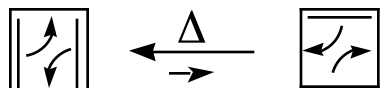
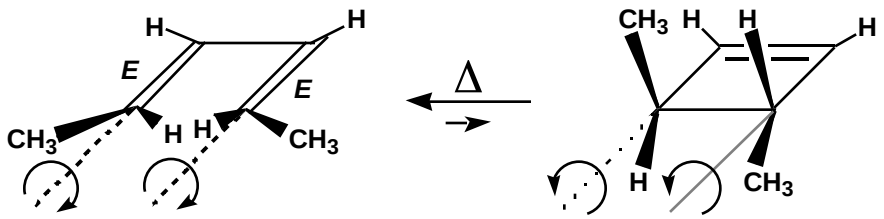
Text Related to Segment 8.06 ©2002 Claude E. Wintner

The entire scheme of Segment 8.05 reverses for the related cases of the thermal and photochemical equilibria between 1,3-butadienes and the corresponding cyclobutenes. The overall course of the thermal interconversion is summarized as follows, using the methyl-substituted example 2*(E)*,4*(E)*-hexadiene to illustrate the *conrotatory* stereochemical outcome. 2*(E)*,4*(E)*-hexadiene equilibrates thermally *only* with *trans*-3,4-dimethylcyclobutene:



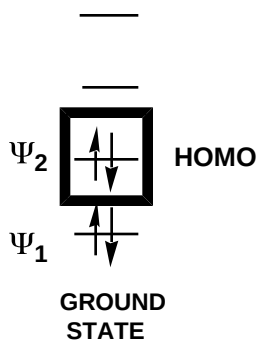


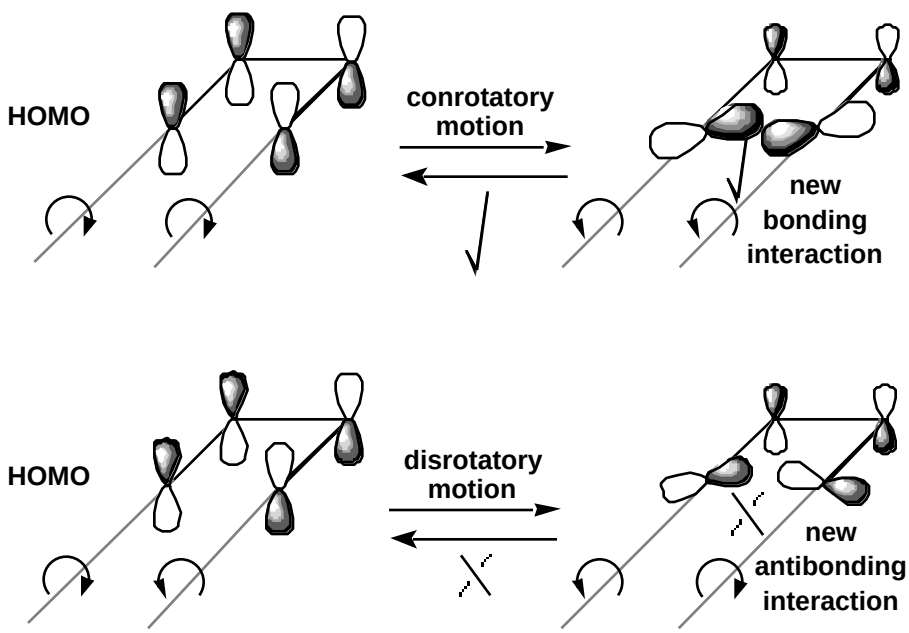
observed stereochemical result for thermal butadiene — cyclobutene interconversion: conrotatory motion

It will be noted that, for steric reasons, such a transformation only can be expected to occur from the *s-cis* conformation of a 1,3-butadiene. Another point to be made here is that the equilibrium in these cases lies on the side of the 1,3-butadienes, because of the strain energy in cyclobutenes. However, this fact has no bearing on the theoretical treatment of the *stereochemical relationship* obeyed within the equilibrium; once again, that association — now the conrotatory one — is adhered to rigorously, and there is no crossing over, so long as the equilibrium is under thermal (and not photochemical) control.

If we once again consider the orbitals involved, the HOMO of butadiene and substituted butadienes — Ψ_2 of Segment 8.01 — only can be transformed into the

required σ orbital in a bonding sense as a result of conrotatory motion; disrotatory motion will lead to an antibonding interaction:

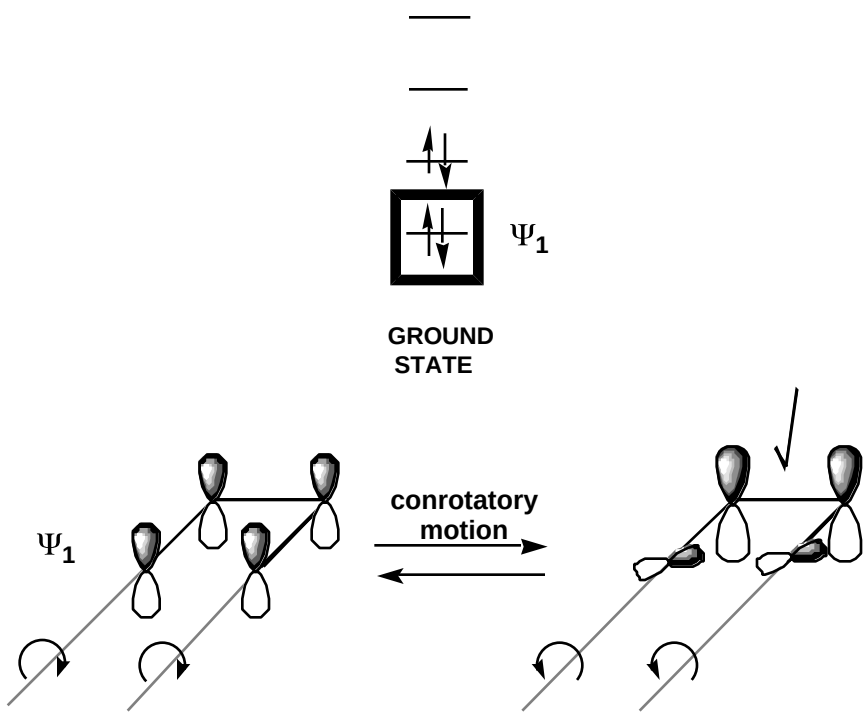




HOMO of ground state butadiene predicts conrotatory motion for ground state (thermal) butadiene — cyclobutene interconversion

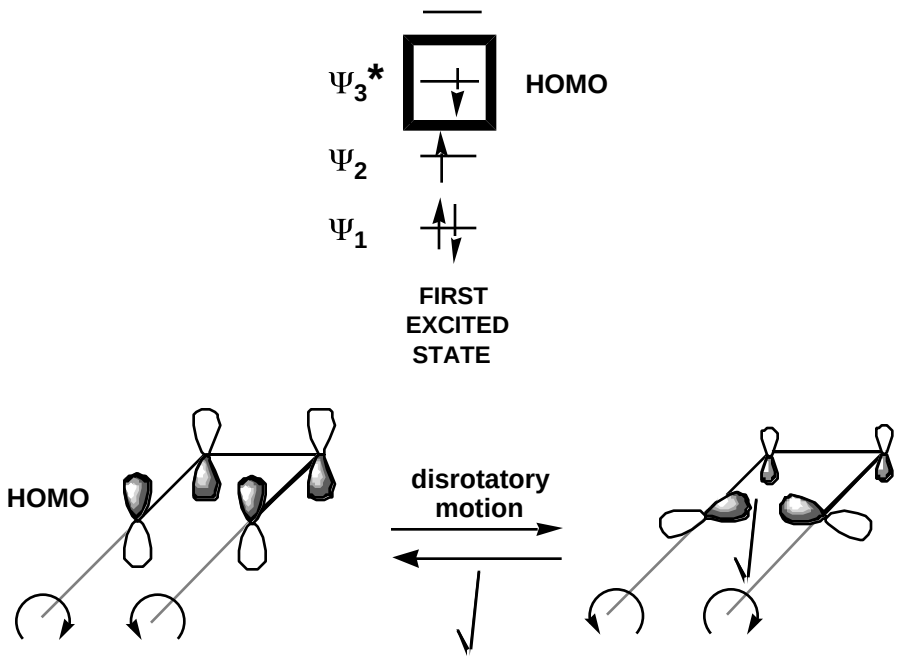
One might ask about the attendant antibonding interaction in Ψ_2 that appears to correlate with the antibonding π^* orbital of the product cyclobutene. However, we must remember that *only two electrons are allowed in any orbital!* Ψ_2 correlates with the new σ bond when the motion is conrotatory. The new π bond comes about as the result of the transformation of Ψ_1. (This gives us just a taste of the treatment

based on examination of the entire orbital array of the starting material as it correlates with the entire orbital array of the product.)



Ψ_1 allows correlation with π in ground state conrotatory butadiene — cyclobutene interconversion

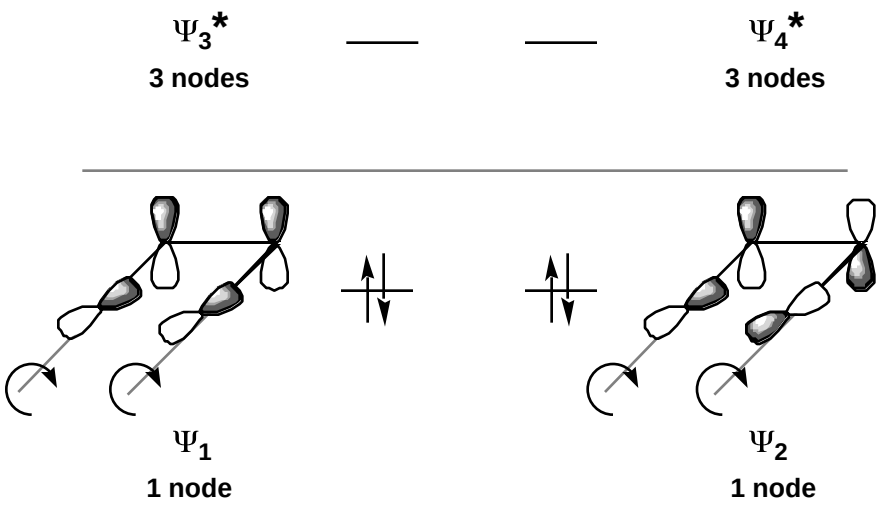
Once again the reversed result is observed under photochemical conditions: 2*(E)*,4*(E)*-hexadiene equilibrates photochemically with *cis*-3,4-dimethylcyclobutene. Now the motion is *disrotatory!* Assuming that the photochemical reaction is initiated by excitation of the substituted butadiene to its first excited state, the HOMO becomes Ψ_3^*, which correctly predicts the observed photochemical result:



HOMO of first excited state of butadiene predicts disrotatory motion for first excited state (photochemical) butadiene — cyclobutene interconversion

What of an interpretation of the butadiene—cyclobutene interconversion in terms of the concept of aromaticity? There is a corollary, the "Möbius corollary," to Hückel's rule. *Continuous cyclic π electron systems containing 4n electrons, where n is an integer, and with orbitals having odd numbers of nodes, possess unusual stability (termed "Möbius aromatic stability"). Conversely, continuous cyclic π electron systems containing 4n+2 electrons, and with orbitals having odd numbers of nodes, are destabilized (termed "anti-aromatic").* Our final figure construes transition state orbitals for the conrotatory thermal butadiene—cyclobutene reaction as Möbius aromatic, having 4n (n=1) electrons and odd nodes. A disrotatory thermal butadiene—cyclobutene transformation would have unfavorable ("forbidden") Hückel-anti-aromatic transition state orbitals, with 4n electrons and zero or even nodes. We should emphasize again that, for these so-called "electrocyclic"

reactions, it is the *transition state* that is aromatic or anti-aromatic. Neither the starting material nor the product is being considered in this connection.



TRANSITION STATE orbitals for conrotatory thermal butadiene — cyclobutene interconversion are Möbius aromatic