10.7: Facial Selectivity

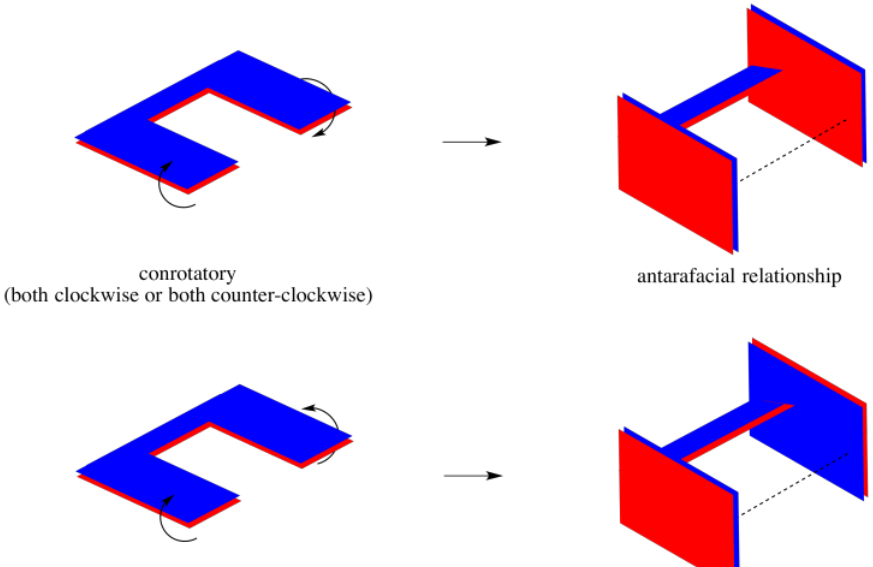
In addition to the consequences of endo- vs. exo- additions in the Diels Alder reaction, pericyclic reactions are subject to additional stereochemical constraints. In this section we will look at more issues of topology, or how the surfaces of the molecules fit together. Although this topic applies to both cycloadditions and true pericyclic rearrangements, we will start by looking at cycloadditions.

So far, we have made the simple assumption that two molecules in a Diels Alder reaction would simply come together in a face-to-face fashion. It is easy to imagine that one molecule would sit above the other as they approach, and form bonds from one face of one molecule to one face of the other molecule. In fact, it often happens that way, and this relationship is called a suprafacial addition.

suprafacial antarafacial

However, sometimes something else happens. Imagine one molecule is able to approach the other at a slight angle, such that it is able to slip in between the ends of the other molecule. A molecule would be interacting with its neighbour not just along one face, but along two. It would form bonds via both its top and its bottom face. This type of addition is called antarafacial. It's not exactly like the cartoon shown above, but to get additional detail we will need to look at molecular orbital pictures.

In a true pericyclic reaarrangement such as a Cope or Claisen rearrangement, similar things can happen. When two ends of a molecule fold in to bond with each other, you can imagine doing so in either of two ways. Maybe the two ends roll towards each other, so that the top face on one end of the molecule connects with the top face on the other. Maybe the top face on one end connects with the lower face on the other end.



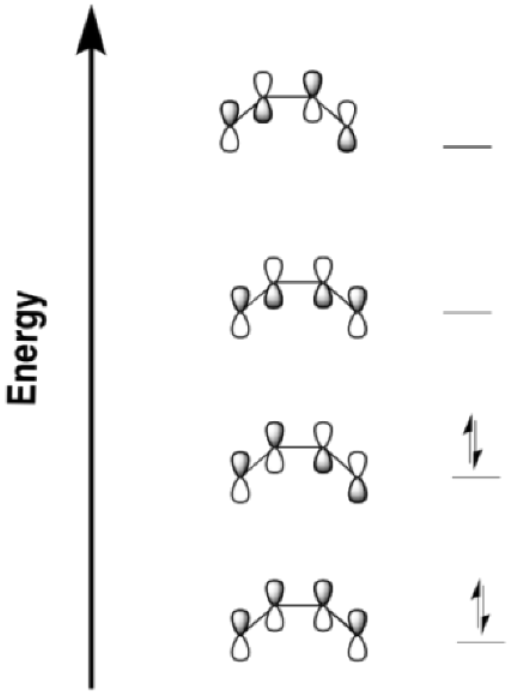
conrotatory
(both clockwise or both counter-clockwise)

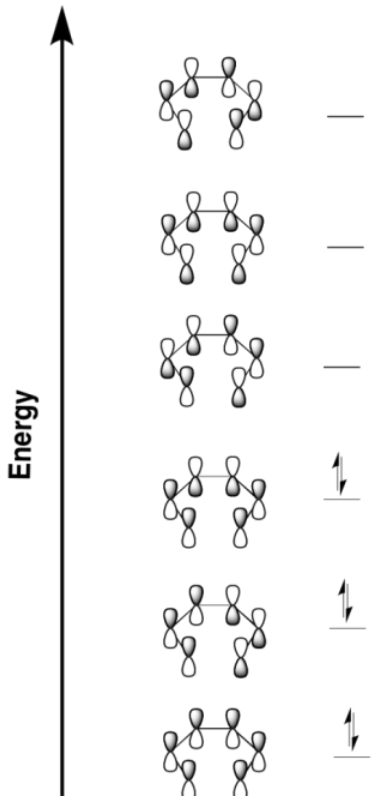
antarafacial relationship

disrotatory
(one clockwise & one counter-clockwise)

suprafacial relationship

Sometimes, the motions that the molecule would undergo to put these interactions in place are called "conrotatory" (rotating together) and "disrotatory" (rotating opposite ways). The interactions they produce, however, are just like the interactions in cycloadditions, with either an antarafacial or a suprafacial relationship, respectively.





Number of electron pairs	suprafacial / disrotatory	antarafacial / conrotatory
even	photochemical	thermal
odd	thermal	photochemical