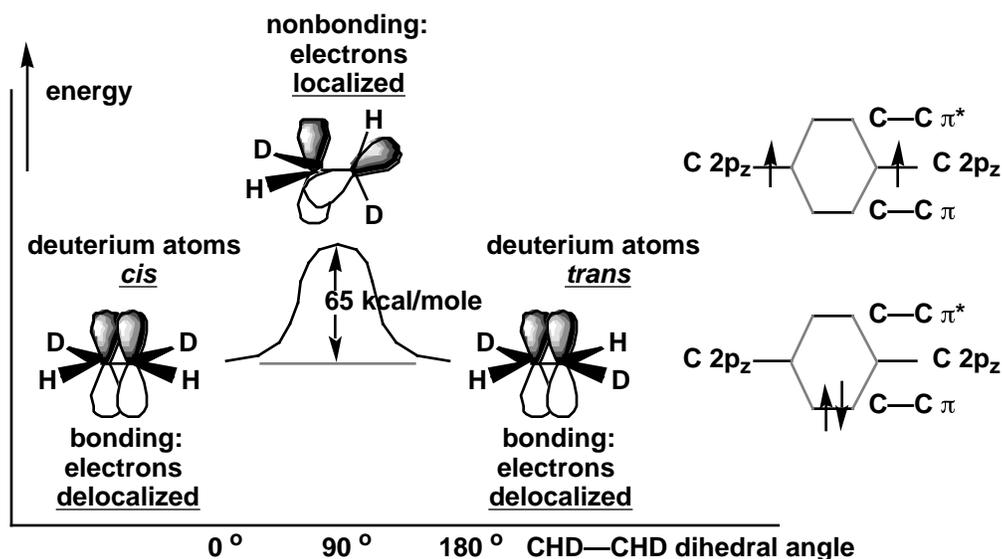


**Text Related to Segment 7.04 ©2002 Claude E. Wintner**

That there is, indeed, a considerable energy advantage to be gained from delocalization in ethylene is immediately suggested by the observed fact that the molecule is planar. Only planar ethylene can have the p orbital overlap necessary to form a delocalized  $\pi$  bond. To examine the other extreme, no p overlap, and no  $\pi$  bond, can be expected from a model of ethylene in which the planes of the two  $\text{CH}_2$  groups, and hence the axes of the two p orbitals, are perpendicular to one another. In other words, in the  $90^\circ$  model the  $\pi$  component of the  $\sigma/\pi$  array is construed as preventing rotation about the carbon-carbon axis (at room temperature), because rotation about the carbon-carbon ( $\sigma$ ) bond in ethylene can be expected to cost the price of the loss of delocalization — the  $\pi$  overlap — of the  $\pi$  bond:



interpretation of the energy of interconversion of *cis*- and *trans*-1,2-dideuterioethylene as the delocalization energy of the  $\pi$  bond in ethylene in the  $\sigma/\pi$  model

In fact, this price has been measured to be about 65 kcal/mole, by observing the interconversion of *cis*-1,2-dideuterioethylene (deuterium atoms on the same side of

the molecule) and *trans*-1,2-dideuterioethylene (deuterium atoms on opposite sides of the molecule), interconversion not being observed until there is an energy input of this magnitude. (The 1,2-dideuterioethylenes must be heated to approximately 500 °C.) This experiment is interpreted to mean that 65 kcal/mole is the energy price paid to achieve the nonbonding, localized orthogonal transition state from the bonding, delocalized ethylenes, by breaking the  $\pi$  bond in the  $\pi$  /  $\pi^*$  model. (It is a frequent source of concern to students that the necessary rotation about the  $\pi$  bond appears to lead to an antibonding  $\pi^*$  state in the product. To understand why this is not actually the case, one should simply concentrate on the nonbonding situation at the top of the energy curve — the transition state — where the p orbitals are orthogonal and there is no  $\pi$  bond. At this point, one considers *not the history* of the orbital array, but its situation at a position of maximum energy. Now, in whichever direction one descends from this position, one moves to achieve a lower energy, that is, bonding situation.)

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