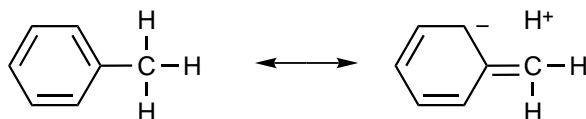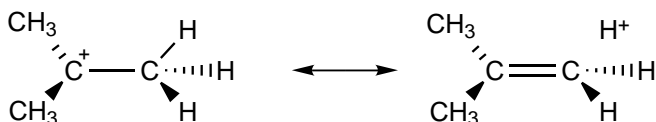**hyperconjugation**

In the formalism that separates bonds into σ and π types, hyperconjugation is the interaction of σ-bonds (e.g. C–H, C–C, etc.) with a π network. This interaction is customarily illustrated by *contributing structures*, e.g. for toluene (below), sometimes said to be an example of 'heterovalent' or 'sacrificial hyperconjugation', so named because the contributing structure contains one two-electron bond less than the normal *Lewis formula* for toluene:

At present, there is no evidence for sacrificial hyperconjugation in neutral hydrocarbons.

The concept of hyperconjugation is also applied to *carbenium* ions and *radicals*, where the interaction is now between σ-bonds and an unfilled or partially filled π- or p-orbital. A contributing structure illustrating this for the *tert*-butyl cation is:

This latter example is sometimes called an example of 'isovalent hyperconjugation' (the contributing structure containing the same number of two-electron bonds as the normal Lewis formula).

Both structures shown on the right hand side are also examples of 'double bond-no-bond resonance'.

The interaction between filled π- or p- orbitals and adjacent antibonding σ* orbitals is referred to as 'negative hyperconjugation', as for example in the fluoroethyl anion:
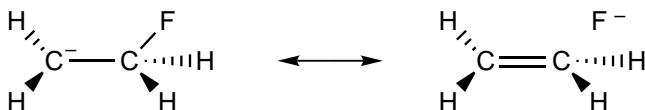
See also *sigma, pi, n-σ* delocalization.*
1994, *66,* 1123