

Conjugation and hyperconjugation

A higher-order bonding interaction between electron orbitals on three or more contiguous atoms in a molecule, which leads to characteristic changes in physical properties and chemical reactivity. One participant in this interaction can be the electron pair in the π -orbital of a multiple (that is, double or triple) bond between two atoms, or a single electron or electron pair or electron vacancy on a single atom. The second component will be the pair of π -electrons in an adjacent multiple bond in the case of conjugation, and in the case of hyperconjugation it will be the pair of electrons in an adjacent polarized σ -bond (that is, a bond where the electrons are held closer to one atom than the other due to electronegativity differences between the two atoms). See CHEMICAL BONDING.

Conjugation. The conjugated orbitals reside on atoms that are separated by a single bond in the classical valence-bond molecular model, and the conjugation effect is at a maximum when the axes of the component orbitals are aligned in a parallel fashion because this allows maximum orbital overlap. Conjugation thus has a stereoelectronic requirement, or a restriction on how the participating orbitals must be oriented with respect to each other. Two simple examples are shown in **Fig. 1**; in 1,3-butadiene ($\text{H}_2\text{C}=\text{HC}-\text{CH}=\text{CH}_2$) conjugation occurs between the p orbitals (π -bonds) of the two double bonds, and in methyl vinyl ether ($\text{H}_2\text{C}=\text{HC}-\text{O}-\text{CH}_3$) the nonbonding sp^3 orbital on oxygen is conjugated with the p orbitals of the double bond. This interaction is manifest in an effective bond order between single and double for the underlined single bond.

If the component orbitals are orthogonal (at right angles) to each other, or if the atoms bearing these orbitals are separated by more than one single bond or by no bond, the molecule is not conjugated. Two examples of molecules which do not exhibit

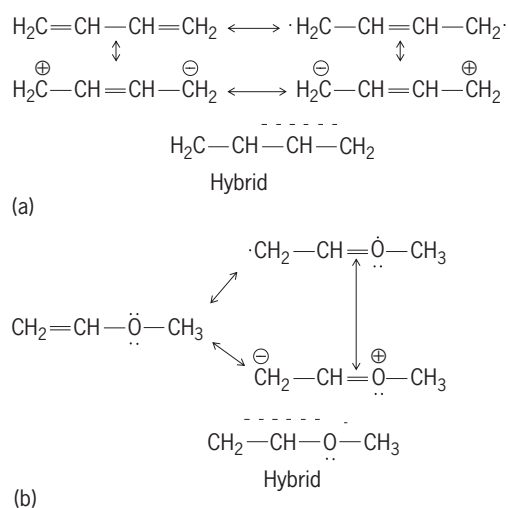


Fig. 1. Conjugated molecules. Broken overbars indicate the effects of conjugation. (a) 1,3-Butadiene. (b) Methyl vinyl ether.

conjugation are 1,4-pentadiene ($\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$) and allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$), the former because there is more than one single bond between the component orbitals and the latter because the component orbitals are orthogonal to each other and are not separated by a single bond.

Chemists have used the conjugation rationale since the midnineteenth century, and it has become well accepted. The valence-bond model of conjugation invokes delocalization: the participating electrons are no longer localized or fixed on a particular atom or between a pair of atoms, but are shared throughout the conjugated orbitals. This increases their entropy, which contributes to a lower overall energy and generally results in greater stabilization for the molecule. From the valence-bond point of view, conjugated molecules are viewed as a weighted average hybrid of two or more valence-bond structures as shown in **Fig. 1** for the two examples. Thus butadiene has a major contribution from the standard valence-bond structure, $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$, but the diradicals or the structures with separation of charge are valid alternative representations, and the same is true for methyl vinyl ether. The effects of conjugation are suggested by the broken lines on the hybrid structures in **Fig. 1**. When more orbital units are linked together or conjugated, more resonance structures can be drawn, and the molecule will be more stable and behave less according to the expectation based on the simple structure drawn from the classical valence-bond model. See DELOCALIZATION; ENTROPY; RESONANCE (MOLECULAR STRUCTURE); STRUCTURAL CHEMISTRY.

Three of the four resonance contributors for butadiene are drawn with only one multiple bond compared to the two multiple bonds in the standard valence-bond structure (**Fig. 1a**); this is known as sacrificial conjugation, in that some bonds in the standard depiction are sacrificed. In methyl vinyl ether (**Fig. 1b**) and in molecules or chemical intermediates, the different pictures drawn for the resonance contributors have the same number of multiple bonds; this is known as isovalent conjugation and results in a greater resonance energy stabilization than in the case of sacrificial conjugation. Other examples of isovalent conjugation include the allyl cation ($\text{CH}_2=\text{CH}-\text{CH}_2^+$ and $\text{C}^+\text{H}_2-\text{CH}=\text{CH}_2$) and benzene.

Conjugation is better understood by considering the molecular orbitals which can be approximated by the mathematical combination of the wave functions for the constituent atomic s and p orbitals (and d orbitals for elements beneath the first row of the periodic table). **Figure 2** shows simple pictorial results of complex molecular orbital (MO) calculations for the π -electrons in butadiene; here the σ bonds are neglected for clarity. The combination of four atomic p orbitals (two each for each of the double bonds) leads to four molecular orbitals. Each of the molecular orbitals is a quartet of “ p -like” orbitals of different size (determined by calculation) situated on the four carbon atoms of butadiene (C^1-C^4). The four π -electrons are placed in these orbitals from the

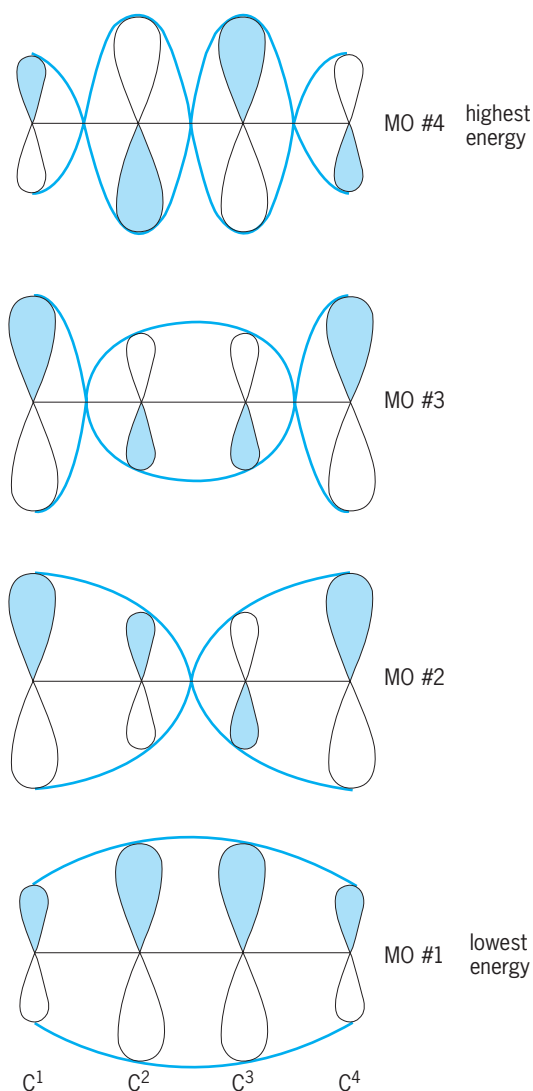


Fig. 2. Molecular orbital (MO) diagram for butadiene as determined by calculation. Algebraic phase is indicated by the presence or absence of tint. Orbital density is depicted as orbital size.

bottom up, so that the two lowest-energy orbitals, MO #1 and MO #2, both contain paired electrons. These two molecular orbitals thus account for the π -bonding in butadiene. In MO #1 the continuous bonding across all four lobes can be seen, with the highest orbital density between C^2 and C^3 . In MO #2 there is a phase change between C^2 and C^3 , with consequent repulsion between the adjacent lobes, but this repulsion is relatively less important because the electron orbital density (depicted as orbital size) is much lower here. In both of these molecular orbitals, the bonding interactions between C^1-C^2 and C^3-C^4 are in phase and add up to strong π -bonds. Thus, the π -delocalization interaction across C^2-C^3 that characterizes conjugation appears very naturally from the molecular orbital description. See MOLECULAR ORBITAL THEORY.

Hyperconjugation. This concept posits the conjugation of polarized σ -bonds with adjacent π -orbitals,

and was introduced in the late 1930s by R. S. Mulliken. This rationale was used to explain successfully a wide variety of chemical phenomena; however, the confusing adaptation of the valence-bond model necessary to depict it and its inappropriate extension to some phenomena led to difficulties. The advent of the molecular orbital treatment has eliminated many of these difficulties.

Early on, hyperconjugation was used to explain the stabilization by alkyl groups of carbocations, or positively charged trivalent carbon. **Figure 3** shows how the orbitals of the σ -bonds of a methyl group (H_3C) exert a hyperconjugative stabilizing effect upon a neighboring p orbital on a methylene group (CH_2). The bonding molecular orbitals of the methyl group utilize aspects of its carbon p orbitals; in both of the conformations or rotations the methyl group has such an orbital which overlaps in phase with the neighboring p orbital on CH_2 . As hydrogen is an electropositive atom, the methyl group acts as an electron donor to stabilize an empty p orbital and to destabilize a filled p orbital on the right-hand carbon. This is in accord with empirical observations. If H^1 is replaced with some other atom X , the hyperconjugative effect of X will be at a maximum in conformation A, where there is orbital density on X , and it will be at a minimum in conformation B, where X is in the nodal or null plane. If X is a more electropositive atom such as silicon, the $C-X$ bond is a donor bond and will stabilize an adjacent empty p orbital, such as in a cation. If X is a more electronegative element such as fluorine, the $C-X$ bond is an acceptor bond and will stabilize an adjacent filled p orbital such as in an anion; this result accords with experiment as well. The donor and acceptor effects are also important where the single p orbital is replaced by a multiple bond. See REACTIVE INTERMEDIATES.

Physical properties and chemical reactivity. The most notable differences in physical properties attributed to conjugation are as follows: (1) The single bonds lying between the two orbital components are shortened. For example, the length of the C^2-C^3 bond in butadiene is 0.148 nanometer, as compared to 0.154 nm for the carbon-carbon single bond in ethane. This shortening can also be explained by the changes in orbital hybridization at these carbons. (2) Electronic absorption spectra begin at significantly longer wavelengths for conjugated than for related unconjugated molecules. (3) Ionization potentials are lower than for isomeric unconjugated

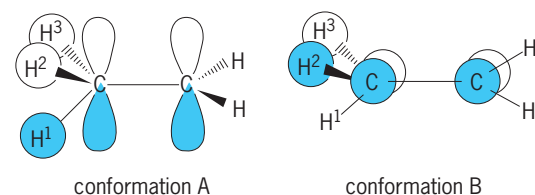


Fig. 3. Diagram showing hyperconjugative effect of orbitals of the σ -bonds of a methyl group (H_3C) on a neighboring p orbital of a methylene group (CH_2). Algebraic phase is indicated by the presence or absence of tint.

molecules. (4) Related to points 2 and 3 is the fact that polarizabilities are larger for conjugated than for the corresponding unconjugated dienes. Polarizability is the ease with which the electron orbitals (electron clouds) of the molecule can be distorted through dipole-dipole interactions with other molecules, ions, atoms, or electrons; it is generally a measure of how loosely the electrons are held by the nuclei. (5) As compared with predictions from formulas for unconjugated molecules, conjugated molecules show lower energies, for example, about 6 kcal/mol (25 kilopascals/mol) lower for 1,3-butadiene than for unconjugated dienes; the excess is describable theoretically as resonance energy (valence-bond picture) or delocalization (molecular orbital theory picture). (6) The magnitude and orientation of dipole moments can be derived from hyperconjugation arguments, although the aforementioned differences in hybridization can also explain this. See BOND ANGLE AND DISTANCE; DIPOLE MOMENT.

In terms of changes in chemical reactivity, the following are exemplary: (1) The acidity of carboxylic acids stems from the conjugation stabilization of their ionized forms. (2) The addition of many chemical reactants takes place across the conjugated system (conjugate addition) rather than at the isolated double bonds, for example, the addition of bromine to butadiene to give a mixture of 1,4-dibromo-2-butene and 1,2-dibromo-3-butene. (3) The well-recognized orientation rules for the addition of

chemical reagents to substituted benzenes and other aromatic systems can be rationalized through conjugated intermediates. (4) The facile formation of an anion from cyclopentadiene and of a cation from cycloheptatriene derives from the conjugation stabilization for those ions. (5) The chemistry of unsaturated organosilicon compounds can be explained only by hyperconjugation effects. (6) Certain changes in chemical reaction rates that occur when hydrogen atoms are substituted by deuterium atoms are clearly hyperconjugative effects.

A number of scientific phenomena depend on the properties of conjugated systems; these include vision (the highly tuned photoreceptors are triggered by molecules with extended conjugation), electrical conduction (organic semiconductors such as polyacetylenes are extended conjugated systems), color (most dyes are conjugated molecules designed to absorb particular wavelengths of light), and medicine (a number of antibiotics and cancer chemotherapy agents contain conjugated systems which trap enzyme sulfhydryl groups by conjugate addition). See VALENCE. Matthew F. Schlecht

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