

❖ Cross Conjugation

The phenomenon of cross-conjugation is a special type of conjugation in a molecule when in a set of three π -bonds only two pi-bonds interact with each other by conjugation, the third one is excluded from the interaction.

Alternatively, we can also say that a system with cross-conjugation has an alkene fragment bonded to one of the central atoms of a 2nd conjugated chain via a single bond. It is different from normal conjugation in which a polyene typically has alternating single and double bonds along with consecutive atoms. Some of the common examples of these types of molecules are given below.

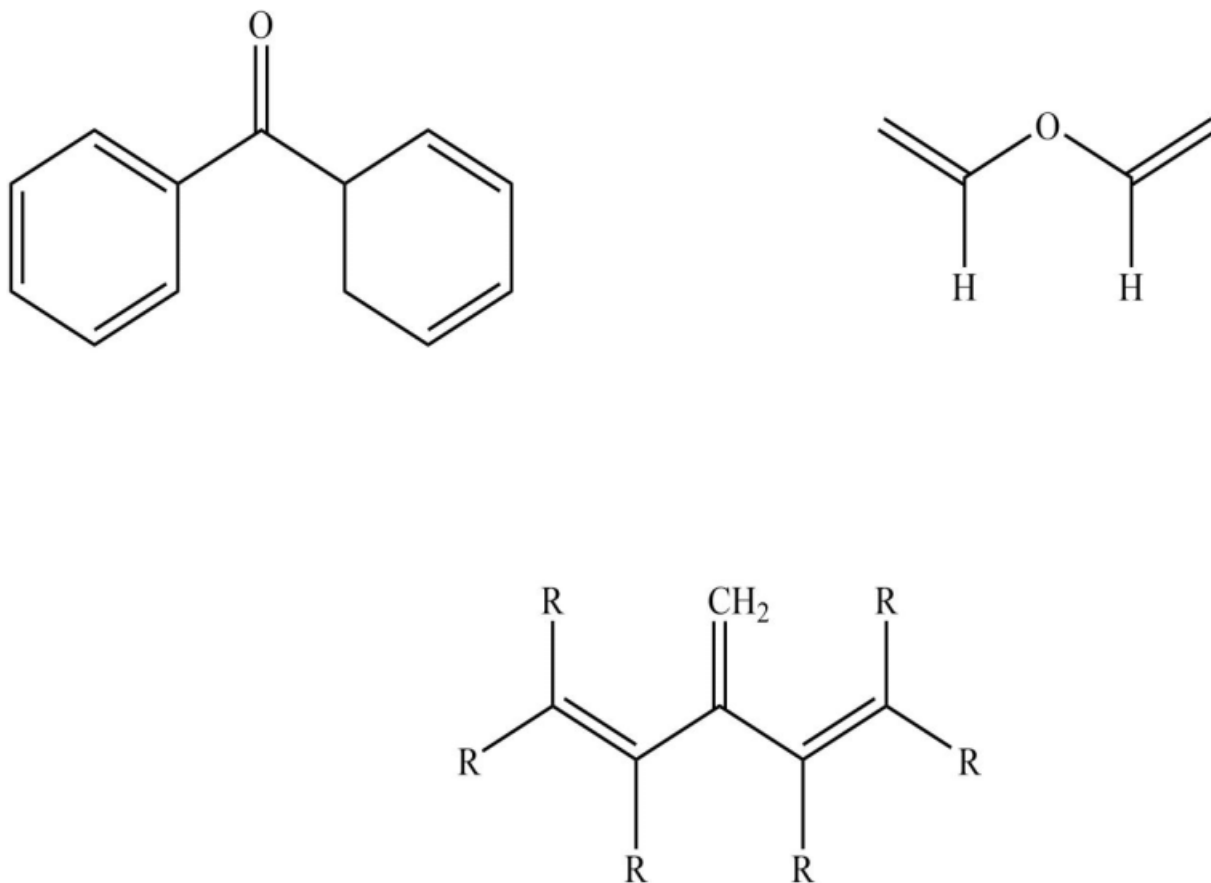


Figure 7. Common examples of molecules with cross-conjugation.

Classically speaking, the branching of double-bonds happens instead of continuous conjugation, and the fragment of that same primary chain is in conjugation with the side group, but all portions are not conjugated with each other very firmly. Common examples of the cross-conjugation effect can be found in molecules such as divinylketones, benzophenone, dendralenes, p-quinones, radialenes, Indigo dye, and fullerene.

Furthermore, it should also be mentioned that the phenomenon of cross conjugation affects the reactivity and molecular electronic transitions in a significant manner. For instance, the lone pair on nitrogen activates the ring at *o*- and *p*-position in aniline (I), supporting the formation of tribromo aniline for bromination reaction. On the other hand, the bromination leads to only monosubstituted acetanilide due to cross conjugation in acetanilide.

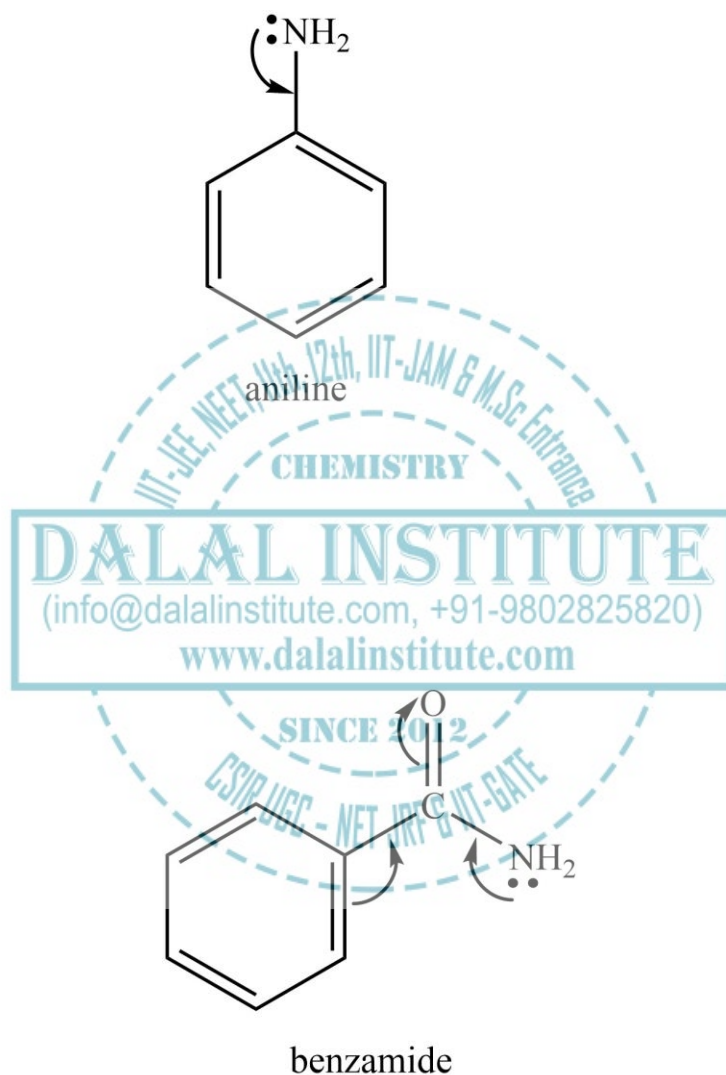


Figure 8. The effect of cross-conjugation upon reactivity.

It is also worthy to note that the phenomenon of cross conjugation is different than homoconjugation- which arises when two π -systems are separated by one non-conjugating group.

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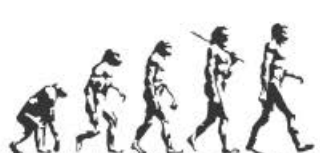
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

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