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TWO-DIMENSIONAL HÜCKEL MOLECULAR ORBITAL THEORY

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Abstract: The simple Hückel molecular orbital theory is extended to include hydrocarbons with sp-hybridization in addition to the sp^2-hybridization. Molecular orbitals are constructed as linear combinations of 2p orbitals in two dimensions perpendicular to each other. Total π bond orders (P) are defined and cover the range up to $P = 2$ in the two-dimensional case. The relationship between bond orders and CC bond lengths is studied. The theory is applied to nine hydrocarbons, which include systems with conjugated and cumulated double bonds as well as triple bonds. Calculated bond lengths from the bond orders are found to agree within ±0.03 Å with experimental values.

INTRODUCTION

The molecular orbital theory for π systems of conjugated hydrocarbons (including aromatics) was introduced by Hückel[1] in 1931, and has since been treated in many text-books[2] and monographs.[3] This theory deals with π systems of hydrocarbons where the C atoms are sp^2-hybridized in the σ system.

In the present two-dimensional application of the Hückel molecular orbital (HMO) theory the hydrocarbon systems are extended to include sp-hybridization. Thus the two-dimensional HMO theory applies to acetylenic (C≡C) systems and those with cumulated C=C bonds.

BASIC PRINCIPLES

The two-dimensional HMO theory is based on linear combinations of atomic 2p orbitals just as the conventional HMO theory,[1-3] but the combinations of 2p orbitals in two directions perpendicular to each other are allowed for. Thus the π system is divided into two parts, say π' and π". It may be assumed, as a simple approximation, that the π' and π" systems are independent of each other, while they of course also are separated from the σ system. In order to deduce the molecular orbitals belonging to the π' and π" systems one may follow the procedure of the conventional HMO theory with all the inherent drastic approximations. Extensions and refinements of the simple HMO theory may also be introduced in the two-dimensional case, but are not treated in this work.

The π-system bond orders are obtainable separately for the π' and π" systems and may be denoted *P'* and *P"*, respectively. The total π bond order (*P*) may be assumed, as the simplest approximation, to be additive: $P = P' + P''$. Hence the total π bond order of C≡C in acetylene becomes $P = 2$ in consistence with the usual convention.[2] In addition we obtain π bond order values quantitatively between $P = 1$ (realized for C=C in ethylene) and $P = 2$.

APPLICATION TO SIMPLE HYDROCARBONS

Figures 1 and 2 show the 2p orbitals of the π systems of (i) diacetylene and (ii) butatriene, respectively. The molecules are C_4 hydrocarbons and exemplify the (i) acetylenic and (ii) cumulated systems. In the first case (i) both of the π' and π" systems may be identified with the 1.3-butadiene system, since only the topology of the carbon skeleton matters in the simplest HMO theory. In the second case (ii) we may take the π' and π" systems as identical to 1.3-butadiene and ethylene, respectively. The figures 1 and 2 include the appropriate π energy levels as

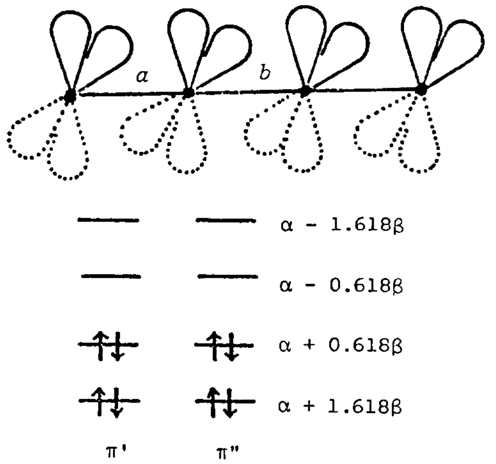

Fig. 1. Diacetylene: 2p orbitals and π-ground state electronic configuration.

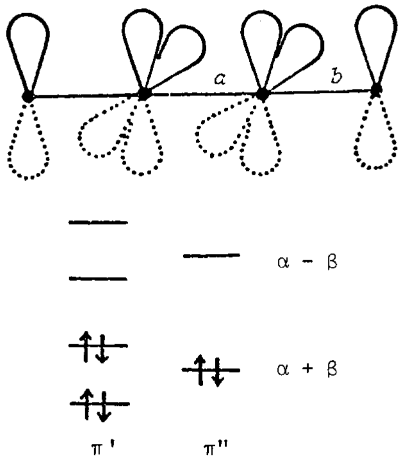

Fig. 2. Butatriene: 2p orbitals and π-ground state electronic configuration.

Table 1. Calculated π bond orders (*P*) and bond distances (*r* in Å).

Molecule	Bond	*P*	*r* calculated	*r* observed	Hybridization
$CH_2{=}CH{-}CH{=}CH_2$	C-C	0.447	1.44	1.463[5]	sp^2-sp^2
$CH{\equiv}C{-}CH{=}CH_2$	C-C	0.447	1.44	1.431[6]	sp^2-sp
$CH_2{=}(CH)_4{=}CH_2$	C-C	0.483	1.43	1.458[7]	sp^2-sp^2
C_6H_6	C$\overset{..}{-}$C	0.667	1.397	1.397[8-11]	sp^2-sp^2
$CH_2{=}(CH)_4{=}CH_2$	C=C middle	0.785	1.37	1.368[7]	sp^2-sp^2
$CH_2{=}(CH)_4{=}CH_2$	C=C terminal	0.871	1.36	1.337[7]	sp^2-sp^2
$CH{\equiv}C{-}C{\equiv}CH$	C-C	0.894	1.35	1.384[12]	sp-sp
$CH_2{=}CH{-}CH{=}CH_2$	C=C	0.894	1.35	1.341[5]	sp^2-sp^2
$CH{\equiv}C{-}CH{=}CH_2$	C=C	0.894	1.35	1.342[6]	sp^2-sp^2
$CH_2{=}C{=}C{=}CH_2$	C=C terminal	0.894	1.35	1.318[13]	sp^2-sp
$CH_2{=}CH_2$	C=C	1.000	1.337	1.337[14,15]	sp^2-sp^2
$CH_2{=}C{=}CH_2$	C=C	1.000	1.34	1.312[16]	sp^2-sp
$CH_2{=}C{=}C{=}CH_2$	C=C middle	1.447	1.27	1.283[13]	sp-sp
$CH{\equiv}C{-}C{\equiv}CH$	C≡C	1.788	1.23	1.217[12]	sp-sp
$CH{\equiv}C{-}CH{=}CH_2$	C≡C	1.894	1.22	1.209[6]	sp-sp
$CH{\equiv}CH$	C≡C	2.000	1.205	1.205[17]	sp-sp

obtained from the conventional HMO theory and expressed in terms of the familiar constants α and β. Also the π-ground state electronic configurations are indicated.

The π bond orders of 1.3-butadiene are known to be $P(C{=}C) = 0.894$ and $P(C{-}C) = 0.447$. Hence we obtain the following total π bond orders: (i) for diacetylene $P_a(C{\equiv}C) = 1.788$ and $P_b(C{-}C) = 0.894$, and (ii) for butatriene P_a(C=C middle) = 1.447 and P_b(C=C terminal) = 0.894.

CC BOND LENGTHS

The present theory may be tested experimentally through a correlation between bond orders and CC bond lengths. It is true that we allow for CC bonds with C atoms in different valence states, *viz.* (a) sp^2-sp^2, (b) sp^2-sp and (c) sp-sp. For the same π bond order one would expect the CC bond length to decrease in the sequence (a) through (c). The experimental data are not consistent to this effect; *cf.* Table 1. Consequently an empirical relationship between P and r (CC bond length in Å) was produced, disregarding the nature of the σ system. The numerical parameters of the Coulson-type formula[4] were adjusted to fit the experimental CC bond lengths of benzene ($P = 0.667$), ethylene ($P = 1$) and acetylene ($P = 2$): $r = 1.557 - 0.220P/[P+0.750(1-P)]$.

Table 1 shows the results of calculations for nine hydrocarbons. Calculated CC bond lengths are compared with observed values.[5-17] The usefulness of the approximate calculations seem to be demonstrated convincingly; the general trends in the bond lengths are well reproduced qualitatively. Furthermore, there is found to be a quantitative agreement between the calculated and observed values within ±0.03 Å.

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