

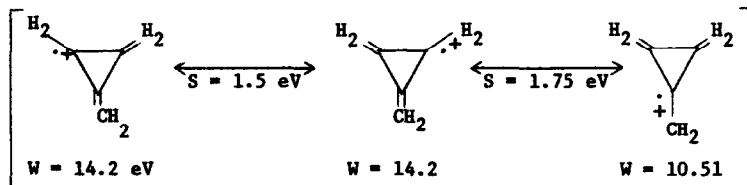
STRUCTURE REPRESENTATION OF HYPERCONJUGATIVE INTERACTIONS FROM PHOTOELECTRON SPECTRA

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(Received in USA 5 April 1974; received in UK for publication 31 May 1974)

The analysis of the photoelectron bands associated with pi-electron ionization of methyl-substituted ethylenes, butadienes and benzenes may be approached using a simple structure representation¹ model invoking only hyperconjugative interaction from the methyl groups. The diagonal elements of the determinants are bond ionization potentials (W's) for the locally ionized structures (W = 10.5 eV ethylene,² 9.07 and 11.46 eV³ for butadiene, 9.25 eV² for the degenerate states of benzene and 14.2 eV⁴ for the pseudo-II structure of a methyl or methylene group). The positions of the stationary states are then determined by the magnitudes of the splitting parameters (S's) which mix the locally ionized structures. The splitting constant for the pseudo II-II interaction ($S_{\Pi, \Pi} = 1.75$ eV) comes from the analysis⁵ of the spectrum of 1,4-cyclohexadiene. The splitting constant for pseudo-II pseudo-II groups is derived from consideration of ethane which suggests $S_{C-H, C-H}^{vic} = 0.8 \cos \theta$, where θ is the dihedral angle between the interacting bonds. This relationship gives $S_{\Pi, \Pi} = 1.2$ eV for the interaction between eclipsed tetrahedral methylene groups. These basic concepts are summarized by the structural representations shown for the case of methylene cyclopropane.^{5a}



For methylated benzenes the interaction constants must be modified according to the atomic density distribution for the arene ion structure. We accommodate this using Huckel densities and the assumption that the atomic density of the vacancy in the olefinic ion structure of cyclohexadiene is $1/\sqrt{2}$. These give equation (1),

$$S_{\Pi''', \Pi_{\text{arene}}} = (\sqrt{2} C_1) 1.75 \text{ eV} \quad (1)$$

where C_1 is the required atomic distribution coefficient at the carbon bearing the substituent.

Finally for 2- and 2,3-dimethyl butadienes a long range interaction between the methyl pseudo Π ionic structure and the nonadjacent olefinic structure (Π_d) is required as recently pointed out by Heilbronner.⁷ We again estimate the magnitude of this interaction parameter (S_{Π''', Π_d}) from comparison of butadiene and cyclohexadiene. The direct (through space) interaction constant for the 1,4 (ene-ene) interaction was 0.7 eV.⁵ The corresponding interaction constant for 1,3-butadiene is 1.20 eV. The S_{Π''', Π_d} interaction constant is $0.7 S_{1,4}$ ⁵ when properly normalized. The results of this treatment, summarized in Table I, are in good agree-



$$S_{\Pi''', \Pi_d} = 0.5 \text{ eV}$$

ment with the observed values. A least squares regression of the observed versus calculated values gives a linear correlation ($IP_{\text{obs.}} = 1.00[IP_{\text{calc.}}] - .004$) with a correlation coefficient of 0.990 (Figure 1).

Our approach is fundamentally different from that of Klessinger⁶ whose HMO treatment of methyl substituted benzenes considered only inductive contributions from the methyl groups. Heilbronner⁷ has recently discussed the problem considering the methyl effect to be the sum of inductive and resonance effects. The present results differ conceptually in that the present hyperconjugative interaction pertains solely to the ionic states. This interaction is totally ignored in the ground states. The parameters used here are derived from the 1,4-cyclohexadiene⁵ spectrum where hyperconjugation is demanded by the assignment. The present model substitutes the transferability property of the parameters (W's and S's) in place of Koopmans' Theorem.

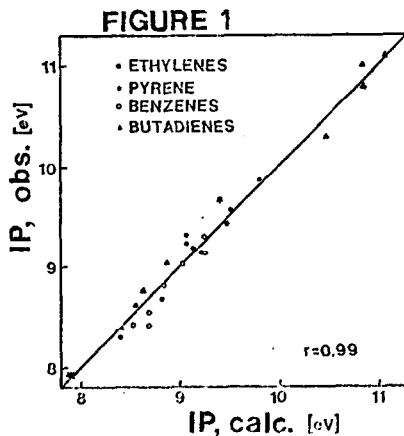


TABLE I

Calc. and Observed Pes Ionization Potentials for Methyl Substituted Ethylenes,
Butadienes and Benzenes.

<u>Compound</u>	<u>Calc. (eV)^a</u>	<u>Observed (eV)</u>	<u>Ref.</u>
Propene	9.81	9.86	14
<u>cis-</u> or <u>trans</u> -2-Butene	9.27	9.32	8
2-Methylpropene	9.27	9.23	7
2-Methyl-2-butene	8.81	8.68	7
2,3-Dimethyl-2-butene	8.40	8.30	2
Methylene cyclopropane ^b	9.52	9.57	2
Methylene cyclobutane	9.14	9.19	2
Methylene cyclopentane	9.22	9.15	2
Cyclobutene	9.48	9.43	9
Cyclopentene	9.14	9.18	9
1,3-Pentadiene	8.75 11.07	8.61 11.1	7
2-Methyl-1,3-butadiene	8.87 (8.75) ^d 10.84 (11.07) ^d	9.04 11.0	10
2,4-Hexadiene	8.42 10.85	8.39 10.8	10
2,3-Dimethyl-1,3-butadiene	8.63 (8.42) ^d 10.48 (10.85) ^d	8.76 10.3	10
Toluene	9.25 (A) 8.84 (S)	9.3 (A) 8.82 (S)	2
<u>m</u> -Xylene	8.69 (A) 9.03 (S)	8.55 (A) 9.03 (S)	11
<u>p</u> -Xylene	9.25 (A) 8.53 (S)	9.14 (A) 8.43 (S)	11
Mesitylene	8.69 (A,S)	8.42 (A,S)	11
2,7-Dimethyl pyrene ^c	7.91 (S) 9.41 (S)	7.92 9.66	12

- a. Using the parameters indicated in the text except where indicated. b. $S_{\text{II}}, \text{II} \approx 1.5$
c. For pyrene the corresponding W 's are 8.26 (S_3) and 9.96 eV (S_2).¹³ d. Calculated with-
out the distant ($C\equiv H_3$) olefin interaction.

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