

use of H<sub>2</sub>O<sub>2</sub> instead of D<sub>2</sub>O<sub>2</sub> in this preparation gave a product which was only ca. 60% deuterated.

3-Methylpentane-2,4-dione was prepared by the action of 1 mol of methyl iodide and 1 mol of sodium pentane-2,4-dionato ion in ethanol.<sup>15</sup> The pure ligand was fractionally distilled at 435 ± 1 K (1 atm) and was shown to be pure by <sup>1</sup>H and <sup>13</sup>C NMR [<sup>1</sup>H NMR shifts in Table V: <sup>13</sup>C shifts relative to Me<sub>4</sub>Si at δ 12.54, 28.86, 61.36, and 205.13 (keto form), and at 21.32, 23.27, 105.03, and 190.63 ppm (enol form)].

**Kinetics.** Reactions were studied at 297 ± 1 K in deuterated solvents, using the stopped-flow attachment for a Bruker WH90 pulse Fourier-transform NMR spectrometer described previously.<sup>5</sup> Complete <sup>1</sup>H NMR spectra were recorded as free induction decays every few seconds after mixing, and after Fourier transformation the decaying *N*-chlorosuccinimide <sup>1</sup>H resonance at δ 2.90 ppm was used to obtain the rate constants. Most reactions were studied under pseudo-first-order conditions with at least a 10:1 ratio of metal complex to *N*-chlorosuccinimide. The pseudo-first-order rate constants were obtained by least-squares analysis from the slopes of plots of ln (peak height or peak integral) vs. time. Because of solubility problems a few reactions were studied under second-order conditions with [complex] = [*N*-chlorosuccinimide]; second-order rate constants were then obtained from the slopes of plots of (peak height)<sup>-1</sup> vs. time. Reaction rates were also checked by following the appearance of the methyl resonance of the chlorinated pentane-2,4-dionato ring to low field of the unchlorinated rings, and good agreement with the value obtained from the decaying *N*-chlorosuccinimide resonance was observed.

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## An Analysis of the Effects of Alkyl Substituents on the Ionization Potentials of *n*-Alkenes

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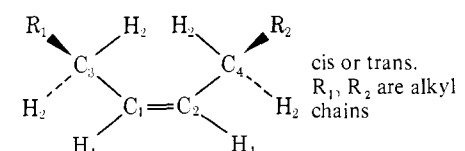
**Abstract:** We report the two highest vertical ionization potentials, as measured by photoelectron spectroscopy, for a large number of straight-chain olefins, and compare these experimental data to the results of molecular orbital calculations by the Fenske-Hall method. It is found that the *cis* and *trans* isomers of a given compound have essentially identical  $\pi$  ionization energies, but some differences are noted for the first  $\sigma$  ones. When these molecules are considered as alkyl-substituted derivatives of ethylene, of the general form R<sub>1</sub>CH=CHR<sub>2</sub>, it is seen that there is a nonlinear decrease in both experimental ionization potentials with alkyl chain length, tending to an asymptotic limit for long substituents. However, the combined effect of two alkyl substituents is not equal to the sum of the effect of each, and the interactions between these two substituents must also be considered. The Fenske-Hall method gives satisfactory correlation with the photoelectron spectral data and their trends and is shown to be useful for interpreting and understanding them.

## Introduction

The usefulness of photoelectron spectroscopy (PES) as a method of measuring some of the vertical ionization potentials (IPs) of a compound has been established by its successful application to many systems.<sup>1</sup> One can also derive empirical rules relating IPs, or their changes over a series of related molecules, to differences in functional groups or geometric conformations.<sup>2</sup> In this work we investigate the IPs of a set of *n*-alkenes and try to determine the effects on them of alkene chain length, position of the double bond, and *cis*-*trans* isomerism. This field of the substituent effects on the IPs of hydrocarbons and their derivatives has been previously investigated by such other workers as Dimeo and El-Sayed,<sup>3</sup> Kinsinger,<sup>4</sup> Maslet et al.,<sup>5</sup> and Carlier et al.<sup>6,7</sup> However, this previous research was incomplete, and we hope to systematize and explain the data for the *n*-alkenes. We are especially in-

terested in looking at trends in these data and in making comparisons throughout the set of compounds and also in meaningful subsets.

In addition, these experiments are supplemented by molecular orbital (MO) calculations on these molecules, to provide a theoretical means for understanding the IPs and their changes. The Fenske-Hall method was chosen for this because it was developed to simulate the results and trends observed from rigorous *ab initio* calculations, but with much less computer time and cost.<sup>8,9</sup> The Fenske-Hall eigenvalues are correlated with the experimental IPs by the application of Koopmans' theorem.<sup>10</sup> Since this theorem assumes that the nuclei remain fixed upon ionization of the molecule, and that the remaining electrons do not reorganize, we report vertical PES ionization energies rather than adiabatic ones. It has previously been demonstrated that this procedure can be used

Table I. Standardized Experimental Bond Lengths and Angles Used for Calculations<sup>a</sup>


Parameter	Value
$d(C_1=C_2)$	1.337 Å
$d(C_1-C_3)$	1.500 Å
$d(C-C)$ in alkyl chain	1.534 Å
$d(C_1-H_1)$	1.083 Å
$d(C_3-H_2)$	1.093 Å
$\angle C_3-C_1-C_2$ trans	124°
$\angle C_3-C_1-C_2$ cis	126° <sup>b</sup>
$\angle H_2-C_3-C_1-C_2$	0°

<sup>a</sup> Both sides of the molecule are treated symmetrically. <sup>b</sup> The value of this angle is slightly larger for the cis isomers than for the trans ones to allow for steric hindrance of the hydrogens eclipsing the double bond.

to calculate IPs which are in satisfactory agreement with the experimental ones for these compounds.<sup>11</sup>

### Experimental Section

**Photoelectron Spectra.** The olefins studied ranged from ethylene to the isomers of *n*-decene. They were purchased from Chemical Samples Co., Phillips Petroleum, and Matheson at a stated purity of 96% or better. Impurity peaks in the liquid olefins (pentenes through decenes) were searched for by gas-liquid chromatography using a Carbowax column and found to be 2% or less. The photoelectron spectra were obtained on a Varian IEE-15 instrument operating in the UV configuration, using the He(I) line at 21.22 eV. Argon was used as an internal standard and resolution check. The width at half-height of the principal argon peak was typically 27 meV. Calibration of the energy scale relative to this peak was done by obtaining the spectrum of methyl iodide and equating its photoelectron IPs with those obtained very accurately from UV spectroscopy.<sup>12</sup> The olefin samples, both gases and liquids, were readily introduced into the spectrometer at room temperature.

**Calculations.** Description of the Fenske-Hall approximate MO method has been given previously.<sup>8,9</sup> The fixed molecular bond lengths and angles used for the olefins are summarized in Table I. These are standardized for the entire series, to facilitate the computations and comparisons among different molecules. These bond lengths and angles are a combination and average of microwave,<sup>13-15</sup> electron diffraction,<sup>16-18</sup> and x-ray diffraction<sup>19</sup> results for both the region about the double bond and the alkyl chains. The bond lengths and angles and conformations chosen are also in accord with theoretical arguments.<sup>20-22</sup> Those for the alkyl chains assume idealized tetrahedral geometry around each carbon atom. The basis functions are atomic Hartree-Fock-Roothaan functions for the free atoms. They are chosen to be consistent with the Mulliken charge and configuration of each atom in the molecular calculation. The carbon functions are those of Clementi,<sup>23</sup> where the 1s and 2s were curve fit to reduce the number of exponents. An exponent of 1.16 was used for the hydrogen 1s function.

### Results and Discussion

The PE spectrum of *trans*-3-nonene is shown in Figure 1. This spectrum is typical for those olefins in the series in which the length of the alkene chain is six atoms or greater and thus is the only spectrum reproduced here. The spectra of shorter olefins, such as ethylene, propene, and *cis*-2-butene, have more distinguishable bands in the 10–18 eV region, and are similar to those displayed previously by other workers.<sup>24-26</sup> We report the experimental vertical IPs in Tables II and III. These were determined with an uncertainty of ca.  $\pm 0.01$  eV for the first band and  $\pm 0.05$  eV for the second one. The first band is the only one with distinguishable vibrational structure for all the

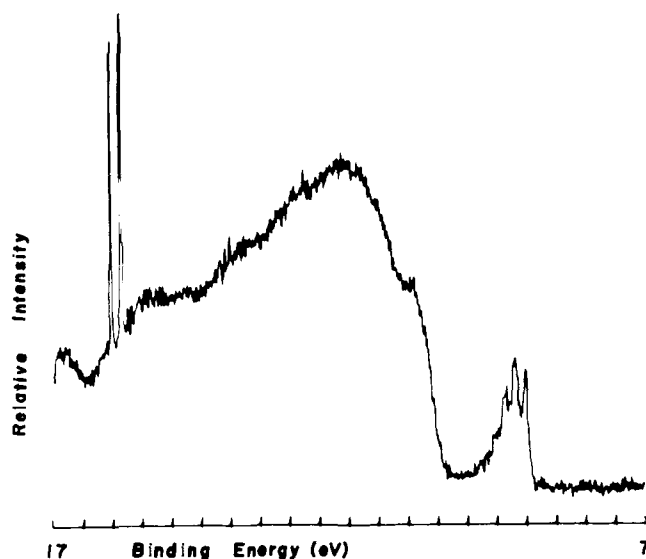
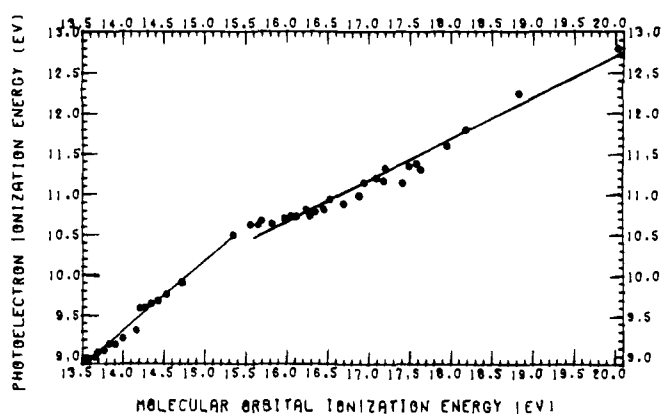
Figure 1. He(I) photoelectron spectrum of *trans*-3-nonene, 17 to 7 eV.

Figure 2. Graph of photoelectron ionization energies vs. IPs calculated by the Fenske-Hall method.

compounds. It is on the basis of this vibrational structure that the first band is assigned to the ionization from the  $\pi$  MO for all the olefins;<sup>5,11</sup> the rest of the peaks will thus originate from  $\sigma$  orbitals.

The PE spectra of these *n*-alkenes are relatively free of background noise, and the peak positions are sufficiently reproducible to be used for the determination of the two highest IPs. However, for the longer olefins there are many broad, overlapping  $\sigma$  peaks in the second region of 10–18 eV. Attempts to deconvolute the spectra in this interval produce ambiguous results. This problem forced us to use only a shoulder on the low-energy side of the second region, rather than a band maximum, for the determination of the first  $\sigma$  vertical IPs of the longer olefins (hexenes through decenes).

Tables II and III contain also the first two IPs for each molecule as calculated from the Fenske-Hall method with Koopmans' theorem. The PES values are plotted against the negatives of the corresponding MO energies, and this graph is shown in Figure 2. The data can be expressed as two straight lines, one for the  $\pi$  molecular orbitals and another distinct line for the  $\sigma$  ones. When fitted by the least-squares method, these lines are represented by the equations

$$IP_{PES} = 0.8737IP_{MO} - 2.925 \text{ (}\pi \text{ ionization energies)} \quad (1)$$

$$IP_{PES} = 0.4880IP_{MO} + 2.869 \text{ (}\sigma \text{ ionization energies)} \quad (2)$$

The correlation coefficients of 0.992 and 0.981 show that the

**Table II.** Trends in  $\pi$  Ionization Energies of the *n*-Alkenes<sup>a</sup>

Molecule	<i>N</i>	R	PES	$\Delta IP/\Delta N$	Fenske-Hall	$\Delta IP/\Delta N$
A. 1- <i>n</i> -Enes HCH=CHR						
Ethylene	0	H	10.50 (10.50, <sup>a</sup> 10.515, <sup>b</sup> 10.51 <sup>d</sup> )		15.34	
Propene	1	CH <sub>3</sub>	9.91 (9.69, <sup>a</sup> 9.744, <sup>b</sup> 10.03, <sup>c</sup> 9.86 <sup>c</sup> )	-0.59	14.71	-0.63
1-Butene	2	C <sub>2</sub> H <sub>5</sub>	9.77 (9.59, <sup>a</sup> 9.625, <sup>b</sup> 9.72 <sup>a</sup> )	-0.14	14.52	-0.19
1-Pentene	3	C <sub>3</sub> H <sub>7</sub>	9.68 (9.524 <sup>b</sup> )	-0.09	14.41	-0.11
1-Hexene	4	C <sub>4</sub> H <sub>9</sub>	9.65 (9.478 <sup>b</sup> )	-0.03	14.34	-0.07
1-Octene	6	C <sub>6</sub> H <sub>13</sub>	9.60	-0.02	14.26	-0.04
1-Decene	8	C <sub>8</sub> H <sub>17</sub>	9.59	0.00	14.21	-0.02
B. <i>cis</i> -2- <i>n</i> -Enes CH <sub>3</sub> CH=CHR						
<i>cis</i> -2-Butene	1	CH <sub>3</sub>	9.32 (9.12, <sup>a</sup> 9.124, <sup>b</sup> 9.36, <sup>c</sup> 9.29 <sup>f</sup> )		14.16	
<i>cis</i> -2-Pentene	2	C <sub>2</sub> H <sub>5</sub>	9.22 (9.036 <sup>b</sup> )	-0.10	13.99	-0.17
<i>cis</i> -2-Hexene	3	C <sub>3</sub> H <sub>7</sub>	9.15 (8.969 <sup>b</sup> )	-0.07	13.89	-0.10
<i>cis</i> -2-Octene	5	C <sub>5</sub> H <sub>11</sub>	9.10	-0.02	13.80	-0.04
<i>cis</i> -2-Decene	7	C <sub>7</sub> H <sub>15</sub>	9.08	-0.01	13.76	-0.02
C. <i>trans</i> -2- <i>n</i> -Enes CH <sub>3</sub> CH=CHR						
<i>trans</i> -2-Butene	1	CH <sub>3</sub>	(9.12, <sup>a</sup> 9.122, <sup>b</sup> 9.37, <sup>c</sup> 9.32 <sup>f</sup> )		14.15	
<i>trans</i> -2-Pentene	2	C <sub>2</sub> H <sub>5</sub>	9.23 (9.036 <sup>b</sup> )		13.98	-0.17
<i>trans</i> -2-Hexene	3	C <sub>3</sub> H <sub>7</sub>	9.16 (8.966 <sup>b</sup> )	-0.07	13.88	-0.10
<i>trans</i> -2-Octene	5	C <sub>5</sub> H <sub>11</sub>	9.09	-0.04	13.79	-0.04
<i>trans</i> -2-Decene	7	C <sub>7</sub> H <sub>15</sub>	9.06	-0.02	13.74	-0.02
D. <i>cis</i> -3- <i>n</i> -Enes C <sub>2</sub> H <sub>5</sub> CH=CHR						
<i>cis</i> -3-Hexene	2	C <sub>2</sub> H <sub>5</sub>	9.15 (8.954 <sup>b</sup> )		13.83	
<i>cis</i> -3-Octene	4	C <sub>4</sub> H <sub>9</sub>	9.05 (8.849 <sup>b</sup> )	-0.05	13.68	-0.08
<i>cis</i> -3-Nonene	5	C <sub>5</sub> H <sub>11</sub>	9.01	-0.04	13.65	-0.03
<i>cis</i> -3-Decene	6	C <sub>6</sub> H <sub>13</sub>	9.01	0.00	13.62	-0.03
E. <i>trans</i> -3- <i>n</i> -Enes C <sub>2</sub> H <sub>5</sub> CH=CHR						
<i>trans</i> -3-Hexene	2	C <sub>2</sub> H <sub>5</sub>	9.14 (8.965 <sup>b</sup> )		13.83	
<i>trans</i> -3-Octene	4	C <sub>4</sub> H <sub>9</sub>	9.03	-0.06	13.69	-0.07
<i>trans</i> -3-Nonene	5	C <sub>5</sub> H <sub>11</sub>	9.01	-0.02	13.65	-0.04
<i>trans</i> -3-Decene	6	C <sub>6</sub> H <sub>13</sub>	9.00	-0.01	13.63	-0.02
F. <i>cis</i> -4- <i>n</i> -Enes C <sub>3</sub> H <sub>7</sub> CH=CHR						
<i>cis</i> -4-Octene	3	C <sub>3</sub> H <sub>7</sub>	9.03 (8.841 <sup>b</sup> )		13.65	
<i>cis</i> -4-Decene	5	C <sub>5</sub> H <sub>11</sub>	8.97	-0.03	13.56	-0.04
G. <i>trans</i> -4- <i>n</i> -Enes C <sub>3</sub> H <sub>7</sub> CH=CHR						
<i>trans</i> -4-Octene	3	C <sub>3</sub> H <sub>7</sub>	9.01 (8.830 <sup>b</sup> )		13.66	
<i>trans</i> -4-Decene	5	C <sub>5</sub> H <sub>11</sub>	8.97	-0.02	13.57	-0.04
H. <i>cis</i> -5- <i>n</i> -Enes C <sub>4</sub> H <sub>7</sub> CH=CHR						
<i>cis</i> -5-Decene	4	C <sub>4</sub> H <sub>7</sub>	8.94 (8.766 <sup>b</sup> )		13.55	
I. <i>trans</i> -5- <i>n</i> -Ene C <sub>4</sub> H <sub>7</sub> CH=CHR						
<i>trans</i> -5-Decene	4	C <sub>4</sub> H <sub>7</sub>	8.95 (8.760 <sup>b</sup> )		13.56	

<sup>a</sup> Reference 27. <sup>b</sup> Reference 5. <sup>c</sup> Reference 24. <sup>d</sup> Reference 25. <sup>e</sup> Reference 28. <sup>f</sup> Reference 29. <sup>g</sup> All IPs are given in eV. The values in parentheses are those of other workers.

agreement is very good. Thus the Fenske-Hall method calculates IPs which are in reasonable agreement with the PES ones for this series of molecules. The selection of the Fenske-Hall method for correlation purposes as compared to MINDO/1 and MINDO/3 has been previously discussed.<sup>11</sup> The effect of orbital reordering on ionization was also investigated and seen not to be a difficulty for the Fenske-Hall calculations. It is the purpose of this present report to elaborate more extensively on the insight of calculations and experiments to illustrate the effects of particular olefin structure on the IPs.

We now wish to interpret these data to understand what effects *cis*-*trans* isomerism, chain length, and position of the double bond have on the IPs. The trends in these factors are especially significant. Such trends are expressed in Tables II and III as  $\Delta IP/\Delta N$ , the variation of ionization energy with the number of carbon atoms in the alkyl chain. We also want to see if the Fenske-Hall IPs follow the same trends as the PES values and predict the structural differences properly. Tables II and III are subdivided according to *cis* and *trans* isomers. The discussions of chain length and position of the double bond

are more easily understood if the following transformation is made. If the olefin is treated as a substituted ethylene R<sub>1</sub>CH=CHR<sub>2</sub>, one can speak instead of the two alkyl chain substituents R<sub>1</sub> and R<sub>2</sub>. Some investigation of this approach has already been done by Kinsinger.<sup>4</sup> Tables II and III are further divided in this manner. Each member of one of these categories has the same general fixed base, R<sub>1</sub>CH=CH, and R<sub>2</sub> is varied. The data for the 1-*n*-enes are graphed in Figure 3; those for the other categories yield similar trends and are not shown here.

When the  $\pi$  IPs of the *cis* and *trans* isomers of a given compound are compared, it is seen that they are equal within error limits for all pairs of molecules studied here, for both experimental and calculated values. This can be understood by examining the  $\pi$  orbital eigenvectors using Mulliken's percent character analysis,<sup>30</sup> which gives a measure of how much a certain atomic basis orbital participates in a MO. The  $\pi$  vectors are predominantly p $\pi$ -p $\pi$  bonding (80% or more) for the two carbon atoms participating in the double bond. There are also contributions from the alkyl chains. Such contributions could cause differences in the IPs. However, they do not in the

**Table III.** Trends in First  $\sigma$  Ionization Energies of the *n*-Alkenes<sup>e</sup>

Molecule	<i>N</i>	R	PES	$\Delta IP/\Delta N$	Fenske-Hall	$\Delta IP/\Delta N$
A. 1- <i>n</i> -Enes HCH=CHR						
Ethylene	0	H	12.79 (12.44, <sup>a</sup> 12.38 <sup>b</sup> )		20.02	
Propene	1	CH <sub>3</sub>	12.24 (11.76, <sup>a</sup> 12.31, <sup>c</sup> 12.22 <sup>d</sup> )	-0.55	18.83	-1.19
1-Butene	2	C <sub>2</sub> H <sub>5</sub>	11.80 (11.30, <sup>a</sup> 11.75 <sup>d</sup> )	-0.44	18.18	-0.65
1-Pentene	3	C <sub>3</sub> H <sub>7</sub>	11.35	-0.45	17.48	-0.70
1-Hexene	4	C <sub>4</sub> H <sub>9</sub>	11.15	-0.20	16.94	-0.54
1-Octene	6	C <sub>6</sub> H <sub>13</sub>	10.73	-0.21	16.10	-0.42
1-Decene	8	C <sub>8</sub> H <sub>17</sub>	10.63	-0.05	15.55	-0.28
B. <i>cis</i> -2- <i>n</i> -Enes CH <sub>3</sub> CH=CHR						
<i>cis</i> -2-Butene	1	CH <sub>3</sub>	11.60 (11.28, <sup>a</sup> 11.65 <sup>c</sup> )		17.94	
<i>cis</i> -2-Pentene	2	C <sub>2</sub> H <sub>5</sub>	11.31	-0.29	17.62	-0.32
<i>cis</i> -2-Hexene	3	C <sub>3</sub> H <sub>7</sub>	11.18	-0.13	17.18	-0.44
<i>cis</i> -2-Octene	5	C <sub>5</sub> H <sub>11</sub>	10.79	-0.20	16.33	-0.42
<i>cis</i> -2-Decene	7	C <sub>7</sub> H <sub>15</sub>	10.67	-0.06	15.68	-0.32
C. <i>trans</i> -2- <i>n</i> -Enes CH <sub>3</sub> CH=CHR						
<i>trans</i> -2-Butene	1	CH <sub>3</sub>	(11.46, <sup>a</sup> 11.96 <sup>c</sup> )		18.04	
<i>trans</i> -2-Pentene	2	C <sub>2</sub> H <sub>5</sub>	11.38		17.58	-0.46
<i>trans</i> -2-Hexene	3	C <sub>3</sub> H <sub>7</sub>	11.20	-0.18	17.09	-0.49
<i>trans</i> -2-Octene	5	C <sub>5</sub> H <sub>11</sub>	10.75	-0.22	16.27	-0.41
<i>trans</i> -2-Decene	7	C <sub>7</sub> H <sub>15</sub>	10.64	-0.06	15.65	-0.31
D. <i>cis</i> -3- <i>n</i> -Enes C <sub>2</sub> H <sub>5</sub> CH=CHR						
<i>cis</i> -3-Hexene	2	C <sub>2</sub> H <sub>5</sub>	11.15		17.41	
<i>cis</i> -3-Octene	4	C <sub>4</sub> H <sub>9</sub>	10.89	-0.13	16.69	-0.36
<i>cis</i> -3-Nonene	5	C <sub>5</sub> H <sub>11</sub>	10.78	-0.11	16.29	-0.40
<i>cis</i> -3-Decene	6	C <sub>6</sub> H <sub>13</sub>	10.71	-0.07	15.94	-0.35
E. <i>trans</i> -3- <i>n</i> -Enes C <sub>2</sub> H <sub>5</sub> CH=CHR						
<i>trans</i> -3-Hexene	2	C <sub>2</sub> H <sub>5</sub>	11.33		17.19	
<i>trans</i> -3-Octene	4	C <sub>4</sub> H <sub>9</sub>	10.82	-0.26	16.44	-0.38
<i>trans</i> -3-Nonene	5	C <sub>5</sub> H <sub>11</sub>	10.72	-0.10	16.11	-0.33
<i>trans</i> -3-Decene	6	C <sub>6</sub> H <sub>13</sub>	10.64	-0.08	15.81	-0.30
F. <i>cis</i> -4- <i>n</i> -Enes C <sub>3</sub> H <sub>7</sub> CH=CHR						
<i>cis</i> -4-Octene	3	C <sub>3</sub> H <sub>7</sub>	10.99		16.89	
<i>cis</i> -4-Decene	5	C <sub>5</sub> H <sub>11</sub>	10.79	-0.10	16.24	-0.32
G. <i>trans</i> -4- <i>n</i> -Enes C <sub>3</sub> H <sub>7</sub> CH=CHR						
<i>trans</i> -4-Octene	3	C <sub>3</sub> H <sub>7</sub>	10.94		16.52	
<i>trans</i> -4-Decene	5	C <sub>5</sub> H <sub>11</sub>	10.70	-0.12	15.97	-0.28
H. <i>cis</i> -5- <i>n</i> -Ene C <sub>4</sub> H <sub>9</sub> CH=CHR						
<i>cis</i> -5-Decene	4	C <sub>4</sub> H <sub>9</sub>	10.81		16.45	
I. <i>trans</i> -5- <i>n</i> -Ene C <sub>4</sub> H <sub>9</sub> CH=CHR						
<i>trans</i> -5-Decene	4	C <sub>4</sub> H <sub>9</sub>	10.73		16.04	

<sup>a</sup> Reference 27. <sup>b</sup> Reference 25. <sup>c</sup> Reference 24. <sup>d</sup> Reference 28. <sup>e</sup> All IPs are given in eV. The values in parentheses are those of other workers.

present cases because, as indicated by the calculations, the contributions are very similar for both members of a *cis*-*trans* pair.

Contrary to a lack of *cis*-*trans* effect on the first IPs, the *cis* or *trans* arrangement of the two alkyl chains does influence the second ones. From the PES data, the first  $\sigma$  ionization energies are smaller for the *cis* isomers of only 2-butene, 2-pentene, 2-hexene, and 3-hexene than for the corresponding *trans* ones. Unfortunately, the calculations are not sufficiently sensitive to predict the correct sequence for the 2-pentenenes, 2-hexenes, and 3-hexenes, because both the experimental and calculated differences are small. The reasons for the *cis*-*trans* ordering of the first  $\sigma$  MOs are not obvious. A proper analysis of this effect would require several more  $\sigma$  IPs, but only one is available experimentally for all these olefins.

An examination of Tables II and III also shows that, generally speaking, the IPs of both  $\sigma$  and  $\pi$  MOs decrease as the chain length of the alkyl substituent R increases. For the  $\pi$  orbitals, this decrease is first seen to be rapid but then diminishes monotonically; changing R from hydrogen to methyl has much more effect than changing it from propyl to *n*-butyl.

Decreases are noted for the  $\sigma$  MOs as well, but the trends differ somewhat from the ones observed for the  $\pi$  orbitals. When the two sets of trends are compared, it is seen that those for the first  $\sigma$  IPs are usually larger in magnitude, are not always monotonically decreasing, and do not achieve a limiting, asymptotic value until the length of the alkyl substituent is longer. The trends in calculated IPs parallel qualitatively those in the PES values. Those for the  $\sigma$  orbitals are not reproduced as well as the ones for the  $\pi$  MOs. Although the magnitudes of the trends are poor, these data can be used semiquantitatively, to see the relative effect of changing an alkyl substituent.

The next step is to determine, if possible, the effect of a particular alkyl chain on the ionization energy. It is hoped that the IPs can be expressed as

$$IP = IP_{\text{ethylene}} + SR_1 + SR_2$$

where SR<sub>1</sub> and SR<sub>2</sub> represent the corrections of R<sub>1</sub> and R<sub>2</sub>, respectively, to the IPs of ethylene. There is however, difficulty with this treatment for the  $\sigma$  MOs. From Table III it is seen that the first  $\sigma$  IPs are different for the *cis* and *trans* isomers. There are thus other factors, such as strain, which must be

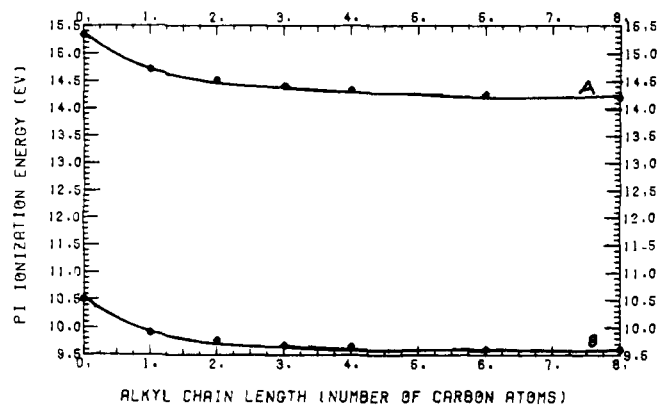


Figure 3. Graph of  $\pi$  ionization energy vs. alkyl chain length for the 1- $n$ -enes. A. Fenske-Hall. B. PES.

Table IV. Contributions of Alkyl Substituents to the  $\pi$  Ionization Energy

Alkyl group	PES, eV	Fenske-Hall
A. Computed from the Symmetric $n$ -Alkenes and the Decene Series		
H	0.00	0.00
Methyl	-0.59	-0.59
Ethyl	-0.68	-0.76
Propyl	-0.74	-0.84
$n$ -Butyl	-0.78	-0.89
$n$ -Pentyl	-0.79	-0.94
$n$ -Hexyl	-0.82	-0.96
$n$ -Heptyl	-0.84	-1.00
B. Computed from the 1- $n$ -Enes		
H	0.00	0.00
Methyl	-0.59	-0.63
Ethyl	-0.73	-0.82
Propyl	-0.82	-0.93
$n$ -Butyl	-0.85	-1.00
$n$ -Hexyl	-0.90	-1.08
$n$ -Octyl	-0.91	-1.13

accounted for, and the IP cannot be expressed in so simple a form. This analysis is therefore done only for the  $\pi$  IPs, which are very close for the two isomers as obtained by both methods. For these MOs the IPs of the cis and trans isomers are averaged in the calculations of the SR values. These parameters are computed in two ways: first, from the symmetric  $n$ -alkenes where the contributions of both alkyl groups are equal, and the series is extended by using the isomers of  $n$ -decene, and second, from the 1- $n$ -enes, where there is only one alkyl substituent to consider. These values of SR are summarized in Table IV and are graphed in Figure 4.

When the results obtained by both methods are compared, it is seen that they are similar but not the same. These results indicate that attempts to assess the effect of a particular alkyl substituent on the  $\pi$  IP cannot be done unambiguously. Different values of SR are obtained for the alkyl chains by the two different methods, from the symmetric alkenes and the decenes or the 1- $n$ -enes. But the two sets of data are qualitatively similar; they show that the decrease in IP is not linear with increasing chain length, but becomes progressively smaller. It finally reaches an asymptotic value. Such trends are observed from both photoelectron and Fenske-Hall IPs, and are similar to those obtained by Kinsinger<sup>4</sup> and Masclat et al.<sup>5</sup>

The fact that one cannot assign a distinct SR value for each alkyl substituent has important consequences. Because one cannot partition the  $\pi$  IP into contributions from an ethylene-like base and two alkyl substituents, the interactions between these three components must be considered. This is a

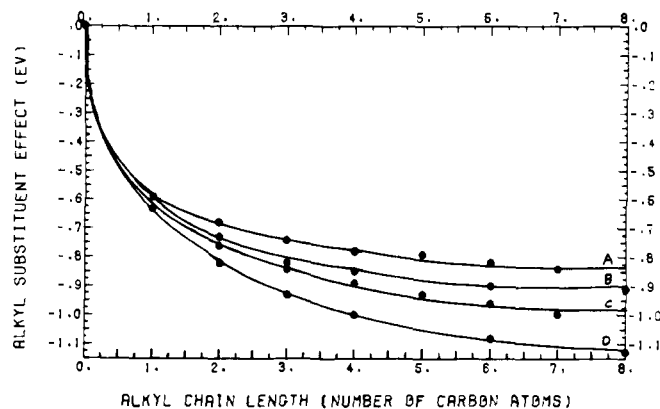


Figure 4. Graph of contributions of alkyl substituents to the  $\pi$  ionization energy. A. From PES values using the symmetric alkenes and decenes. B. From PES values using the 1- $n$ -enes. C. From Fenske-Hall values using the symmetric alkenes and decenes. D. From Fenske-Hall values using the 1- $n$ -enes.

consequence of the delocalization of the  $\pi$  MO. As was mentioned earlier, a clear separation between  $\pi$  and  $\sigma$  interactions does not exist. Rather, the  $\sigma$  vector extends over not only the two double-bonded carbon atoms but the alkyl chains as well. Such an outcome is not really unexpected because it was seen that such a partitioning was not possible for the  $\sigma$  IPs because of cis-trans differences; in these molecules, generally of low symmetry, there is usually no symmetry distinction between  $\sigma$  and  $\pi$  orbitals. Atomic basis orbitals from atoms either in the alkyl chains or in the region of the double bond may belong to the same irreducible representation of the molecular point group, and thus may mix in the eigenvectors. Also, examination of Tables II and III shows that the trends in IPs depend on the constant environment  $R_1CH=CH$  as well as on the alkyl substituent  $R_2$ .

## Conclusion

In this paper we have established trends in the first two ionization energies of the  $n$ -alkenes, and those predicted theoretically by the Fenske-Hall method agree qualitatively with those measured experimentally by PES. An attempt was made to interpret these trends of the  $\pi$  MO in terms of alkyl substituents on ethylene, but the findings indicate that such an analysis in terms of this classical picture is not entirely satisfactory. This arises from the delocalized nature of the electrons in the  $\pi$  bond. Further research in this field may involve the use of the Fenske-Hall method to interpret trends in the PES data of branched olefins and also of various olefin derivatives.

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## Electronic States of Organic Molecules. 6. Analysis of Infrared Intensities. The Hybrid Orbital Rehybridization Model. Charge Distribution in Molecules<sup>1</sup>

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**Abstract:** A general model for analysis of infrared intensities is proposed and applied to a series of organic molecules. This model, called the hybrid orbital rehybridization model (HORM), splits the infrared intensity into a static term due to geometric reorientation of the bond moments and a dynamic term arising from bond rehybridization. A linear dependence between CH bond moments and % s character is observed, and explicit formulas are proposed for the rehybridization components. Criteria for determining which vibrational modes are purely geometric are developed, then used in conjunction with ab initio calculations to obtain values of the CH and CC bond dipoles for series of compounds. Charge distributions in these molecules are also deduced from these results.

### I. Introduction

The positions and intensities of infrared bands potentially contain a great deal of information about both static molecular structure and normal vibrations. However, while much progress has been made in extracting information from line positions,<sup>2</sup> the corresponding analysis of intensities is generally quite crude.<sup>3</sup> In the case of line positions, the harmonic oscillator model provides a reasonable physical picture for qualitative and quantitative analysis. On the other hand, the results of previous analyses<sup>3</sup> suggest that the most obvious parameters for infrared intensities—effective bond moments and atomic charges—do not provide an internally consistent basis for interpretation. Various other types of parametrization have, in fact, been able to reproduce experimental intensities, but they generally lack physical interpretation or are not easily generalized.<sup>3</sup>

In the present work, a general model for infrared intensities which overcomes these difficulties is proposed. This model separates the intensity into a static term due to effective bond moments, and a dynamic term arising from charge rearrangement. Both terms are shown to be functions of the hybridization, and explicit expressions for their evaluation are proposed. The key element in the derivation of this model is a combination of extended basis ab initio intensity calculations with the experimental intensities of small hydrocarbons. One of the more important results of this method is the development of a set of criteria which characterize vibrations whose intensity is due to purely geometric rearrangement of the bond moments.

These criteria, coupled with the fact that such vibrations will be the most intense, provide a powerful tool for the analysis of infrared spectra.

A proper presentation of this model requires a somewhat detailed review of the previous work on infrared intensities, and this is given in section II. In section III, the general hybrid orbital rehybridization model (HORM) is developed, while specific evaluation of parameters is considered in section IV. The use of ab initio localized molecular orbitals to obtain bond moments is treated in section V, while in section VI bond moments calculated with HORM are compared with additional experimental estimates.

### II. Theory and Previous Work

The experimentally measured quantity corresponding to the infrared intensity is the absolute absorption coefficient.  $A_i$ . For a transition from the  $i$ th to the  $i + 1$  vibrational state, it is given by

$$A_i = \frac{8\pi^2 N \nu_i}{3hc} \sum_i g_i |\langle i+1 | \mu | i \rangle|^2 \quad (1)$$

where  $N$  is Avogadro's number,  $\nu_i$  is the transition frequency,  $h$  is Planck's constant,  $c$  is the velocity of light, and  $\mu$  is the dipole moment operator. The sum on  $i$  is over the  $g_i$  degenerate states. Under the assumption of electrical and mechanical harmonicity,  $A_i$  becomes<sup>4</sup>

$$A_i = \frac{N\pi g_i}{3c^2} \left| \frac{\partial \mu}{\partial Q_i} \right|^2 \quad (2)$$