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THE VACUUM ULTRAVIOLET SPECTRA OF CYCLOHEXANE, CYCLOHEXENE,  
1,4-CYCLOHEXADIENE, ISOTETRALIN, AND SEVERAL  
METHYL SUBSTITUTED ANALOGS

THESIS

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By

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A paucity of literature exists on the Independent System analysis of adjacent, parallel transition dipoles. Applying this theory and certain spectral information semi-empirical calculations were made to predict absorption profiles and band intensities.

To aid in the assignment of the  $\pi^* \leftarrow \pi$  absorption bands it was necessary to obtain the vacuum ultraviolet spectra of cyclohexane and cyclohexene. Because the spectra of these molecules contained sharp, atomic-like absorption bands a Rydberg series could be fitted to certain absorptions, thus the determination of their ionization potentials.

Using Independent System analysis profiles and intensities of  $\pi^* \leftarrow \pi$  absorption bands in several methyl substituted 1,4-cyclohexadienes and isotetralin were predicted where general agreement was found with observed experimental spectra.

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## CHAPTER I

### INTRODUCTION

Electronic absorption spectra of molecules are commonly recorded in the visible and ultraviolet spectral regions of liquid samples in a suitable matrix. To record spectra at energies above the ultraviolet region additional experimental features must be considered. First, the monochromator must be in a vacuum because at these higher energies atmospheric gases absorb radiation therefore being responsible for this spectra region being designated as the vacuum ultraviolet (VUV). The higher energy limit in the VUV is determined by the transmitting properties of materials used for sample cell windows, if gaseous samples are being investigated. For example, if the windows are lithium fluoride, the limit is  $1100 \text{ \AA}$  (angstroms) and for calcium fluoride,  $1250 \text{ \AA}$ . Additional problems associated with this spectral region are concerned with a high intensity light source, a highly efficient monochromator, and, if possible, a detection system which can provide the data in terms of the absorbance of the material. Instrumentation of this type, which needs further improvement, is available for investigating electronic absorptions associated with high energy excitations. Examples of such high energy excitations described in terms of molecular orbitals are  $\sigma^* \leftarrow \sigma$ ,  $\pi^* \leftarrow \pi$ ,

$\sigma^* \leftarrow \pi$ , and Rydberg excitations. The emphasis of this paper is placed upon the energy and assignment of these types of transitions for a family of compounds in the vacuum ultraviolet spectral region.

The work contained herein has been divided into two major parts. The first part describes the VUV spectra of cyclohexane, cyclohexene, and 1,4-cyclohexadiene; designation of their Rydberg bands; and values of their first ionization potentials. These spectral values are compared with adiabatic and vertical ionization potentials determined by other experimental methods.<sup>1,2</sup> Part of the discussion is devoted to the description of Rydberg orbital types that are associated with the absorptions for each series. Emphasized are the differences in the origin of the excited electron in cyclohexane and cyclohexene, a  $\sigma$  orbital in the first and a  $\pi$  orbital in the latter. This is reflected in the 'term values' of their Rydberg series.

One of the first compounds to be investigated using Rydberg series analysis of vacuum ultraviolet spectra was ethylene.<sup>3</sup> He observed that this compound's spectra contained a number of sharp, atomic-like bands much like Rydberg bands commonly seen in atomic spectra. From these particular bands he 'fitted' a series to their respective energies according to the Rydberg equation:

$$IP = \bar{\nu}_n (\text{cm}^{-1}) - R_\infty / (n - \delta)^2$$

where IP is the ionization potential,  $\bar{\nu}$  is the observed

band energy,  $R_{\infty}$  is the upper limit of the Rydberg constant with increasing nuclear mass,  $n$  is the integer quantum number and  $\delta$  is the quantum defect number. The quantum defect number varies in value for a Rydberg series and is related to the type of Rydberg orbital (whether it be an  $s$ ,  $p$ ,  $d$ , etc.) to which the transition is occurring. Adapting the Rydberg equation to the electronic spectra of molecules such as cyclohexane, cyclohexene, and 1,4-cyclohexadiene is beneficial in that it provides the most accurate method for the determination of ionization potentials when compared with data from photoelectron spectroscopy and photoionization methods. In addition, electronic spectra contain vibrational envelopes which can be used to calculate geometrical information about excited or ionized states of a molecule.

The results of molecular orbital calculations<sup>5</sup> are included in the first part to determine relative energies of the  $\pi$  orbitals in 1,4-cyclohexadiene whose symmetries are determined by inspection of the coefficients in the LCAO-MO's. The methylene groups in this molecule are of the proper symmetry to interact with the  $\pi$  and  $\pi^*$  orbitals; therefore, their relative molecular orbital energies are shifted after interaction at the unperturbed energies. This coupling mechanism is described as an indirect interaction mechanism.<sup>6,7</sup> Direct interaction of the olefin groups in 1,4-cyclohexadiene is suggested to occur via direct overlap of the atomic  $p$  orbitals through space from the non-conjugated  $\pi$  orbitals. Both



effects of direct and indirect interaction are taken into account to predict an energy diagram of the  $\pi$  orbital system.

The second part of this work is concerned with the possible application of a theoretical model to account for intensity profiles, the fundamental feature of this model being that localized excitations within a molecule interact via transition dipoles.<sup>8</sup> Therefore, two localized excitations can interact in two different manners either constructively or destructively. If these transition dipoles are analogous to classical dipoles, then the interaction can be specified in terms of the natural energies of the individual transitions, the magnitudes of the vectors associated with the transition dipole and distance separating the dipoles. The intensities of the resulting energies are predicted to be the vectorial additions of the vectors associated with the specific transition dipoles. The model is applied by using experimental values to determine certain parameters while the spectral results for other molecules are predicted. The success upon the application of this theoretical model to a system of transition dipoles is then gauged by comparing the predicted intensity profile with that observed.

The basic assumption for the application of this model is that the excitations of interest are localized. This is the reason that for certain molecules like 1,3-butadiene the model does not agree well with the experimental values to the extent desired.<sup>9</sup> However, it has been noted that the model's

predictions are in agreement with the experimental findings for a series of methyl substituted allenes thus the spectra of another series of compounds was of interest to evaluate the model for such excitations.

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## CHAPTER II

### EXPERIMENTAL

#### Spectrophotometer and Sampling

Vacuum ultraviolet spectra (1200-2000 angstrom) were obtained with a one-meter McPherson spectrophotometer with a windowless Hinteregger hydrogen discharge lamp source and a 10 centimeter sample cell as has been previously described.<sup>1</sup> Sample preparation and purification were accomplished using standard vacuum line techniques. Each sample was purified by repeated freeze-thaw cycles until a sharp melting point was obtained and then transferred into the absorption cell for recording the spectra. The absorption cell was equipped with either calcium fluoride or lithium fluoride windows, 2 mm x 1 inch diameter. The pressures of gaseous samples were measured with an MKS Baratron Capacitance manometer (type 144) which was calibrated against a McLeod gauge over the pressure range of interest. The spectral wavelengths (accurate to  $\pm .25 \text{ \AA}$ ) were corrected against the hydrogen lamp spectra where the ' $\alpha$ ' line of the Lyman series at  $1215.7 \text{ \AA}$  was used for calibration. Without sample in the cell, a baseline was recorded upon which the VUV absorption spectrum was then superimposed. Corresponding adjustments were then made for all absorbance readings.

### Experimental Oscillator Strengths

In order to compare experimental with predicted intensities of designated absorption bands, it is necessary to integrate the area underneath these bands in terms of three dimensional oscillator strengths<sup>2</sup> defined by the equation:

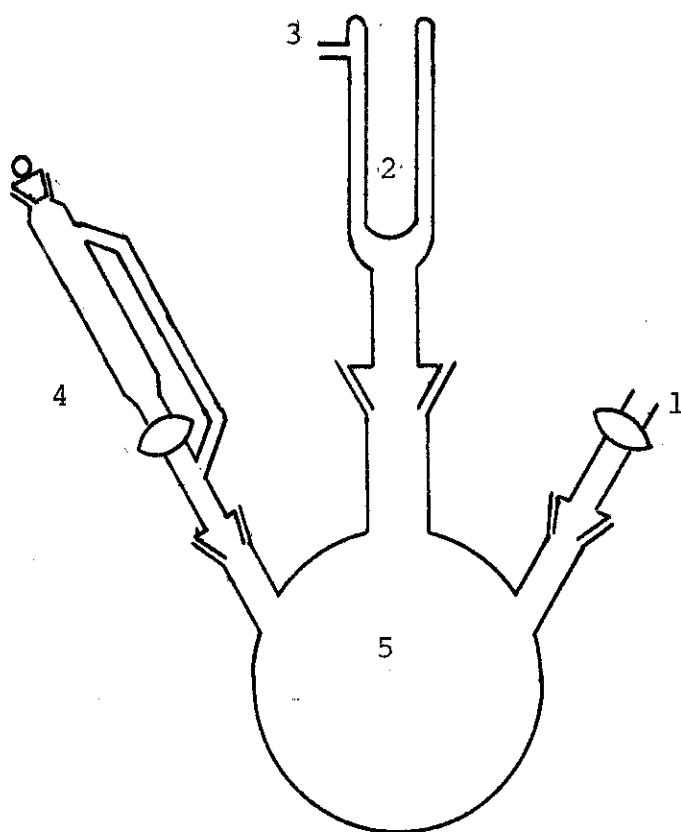
$$f = 4.32 \times 10^{-9} \int \epsilon(\bar{\nu}) d\bar{\nu}.$$

To convert the band intensities into oscillator strengths (f) the absorbance and wavelength must be converted to molar absorptivity and energy units, respectively. Once converted the area can then be determined by various methods. If the band assumes a symmetrical gaussian or a parabolic shape, then a function can be fitted to the band and integrated mathematically. Another means of determining the band area is to use an appropriate method from numerical analysis.<sup>3</sup> A third method of integration is to integrate 'gravimetrically' by weighing the replotted band of the absorption curve against a known standard of which the area and weight are known accurately. The latter two methods were used with the aid of a FORTRAN IV computer program and CALCOMP plotter to calculate oscillator strengths where values by both methods were compared against one another. Absorbance and wavelength data were taken from the recorded spectra every ten angstroms and with this program, the oscillator strengths(f) were determined using the trapezoidal rule. The CALCOMP line plotter produced a replotted spectra in the desired energy units. These replotted bands were then integrated 'gravimetrically' and

compared with the oscillator strengths calculated using the trapezoid rule. Agreement between the results of the two methods was within  $\pm 5\%$ . This deviation is comparable with experimental uncertainties such as pressure readings ( $\pm 10\%$ ).

#### Source of Sample Compounds

Cyclohexane, cyclohexene, 1-methylcyclohexene, 1,2-dimethylcyclohexene, 1,4-cyclohexadiene, and 1-methyl-1,4-cyclohexadiene were obtained from Peninsular Chemresearch which designated the purity as 99+%. Isotetralin also obtained from Peninsular Chemresearch was of 95+% purity. Samples of 1,2-dimethyl-1,4-cyclohexadiene and 1,5-dimethyl-1,4-cyclohexadiene were synthesized by the Birch reduction of ortho- and meta- xylene, respectively.<sup>4</sup> In the synthesis of these compounds the reaction vessel of the apparatus (Figure 1) is first charged with 400 milliliters of tetrahydrofuran which was thoroughly dried by refluxing over phosphorous pentoxide and then sodium for approximately one hour. Approximately one and one-half grams of fractionally distilled ortho- or meta-xylene depending upon the product desired is added to the reaction vessel. The condenser is supplied with a mixture of dry ice and acetone. The system is then flushed with dry nitrogen for 15 minutes and then ammonia is condensed into the reaction flask for one hour. Two milliliters of dry ethanol and approximately one-fourth gram of freshly cut sodium are



## LEGEND

- 1 Inlet for dry nitrogen or ammonia
- 2 Cold finger filled with dry ice and acetone
- 3 Exit to mercury bubbler
- 4 Dropping funnel containing dry ethanol
- 5 Reaction flask (insulated with glass wool and aluminum foil)

carefully added at fifteen minute intervals for one hour. Following the last addition of sodium the reaction is continued for another hour to insure conversion of the starting compound. The reaction is then quenched dropwise with distilled water and the product is then purified by distillation with a rotary evaporator.

#### Structural Confirmation of Synthesized Compounds

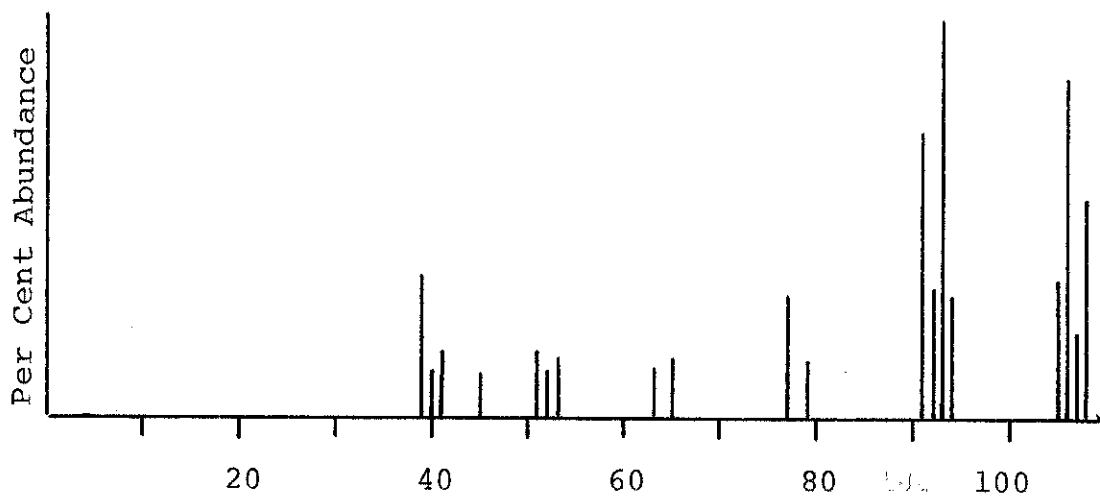
The structure of these two dimethyl substituted 1,4-cyclohexadienes were confirmed by nuclear magnetic resonance (nmr) and mass spectra. The protons of the two methyl groups for both molecules were indicated by one large singlet band located at a chemical shift ( $\delta$ ) value of 1.8. There were no bands located in the chemical shift range ( $\delta \approx 6.5$  to 8.0) observed for the protons of benzene. This indicates that the reactant whether it be ortho- or meta- xylene was essentially converted to a 1,4-cyclohexadiene. In addition, the integration of the nmr spectra for these two molecules indicated the methyl protons constituted  $50 \pm 3\%$  of the total area. This is predicted for the chemically pure products.

The molecular structure of these two synthesized compounds was further confirmed by mass spectra using an ionization energy of 70 electron volts. The mass spectra and corresponding bar graphs of 1,2- and 1,5- dimethyl-1,4-cyclohexadiene are given in Figure 2 and Table 1. The mass spectra of these compounds produced m/e (mass/charge) ions of 108, the



Figure 2. Bar Graphs of Mass Spectra for 1,2-Dimethyl-1,4-Cyclohexadiene and 1,5-Dimethyl-1,4-Cyclohexadiene

1,2-DIMETHYL-1,4-CYCLOHEXADIENE



1,5-DIMETHYL-1,4-CYCLOHEXADIENE

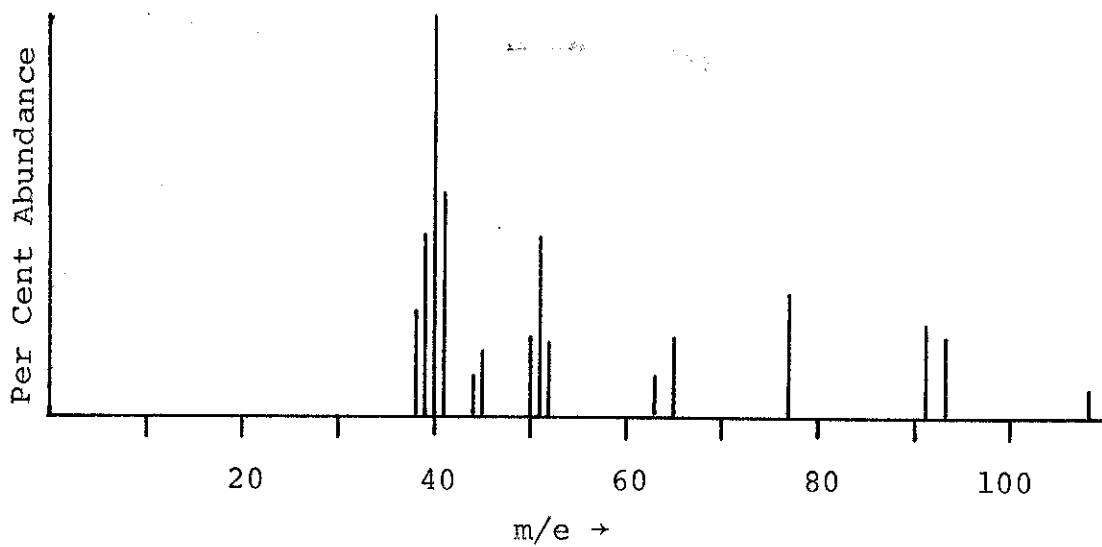


TABLE I

MASS SPECTRA OF 1,2- AND 1,5- DIMETHYL-1,4-CYCLOHEXADIENE  
WITH ABUNDANCES RELATIVE TO BASE PEAK

## 1,2-DIMETHYL-1,4-CYCLOHEXADIENE

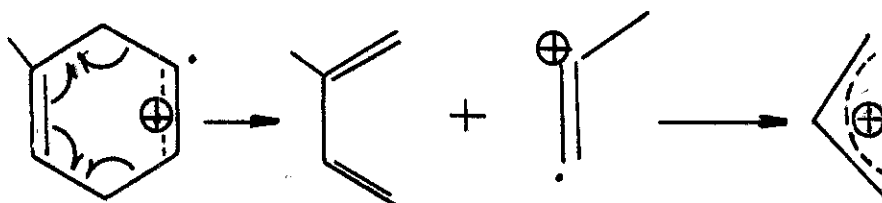
m/e	Abundance	Ion	m/e	Abundance	Ion
108	55	C <sub>8</sub> H <sub>12</sub>	65	15	C <sub>5</sub> H <sub>5</sub>
107	22	C <sub>8</sub> H <sub>11</sub>	63	11	C <sub>5</sub> H <sub>3</sub>
106	85	C <sub>8</sub> H <sub>10</sub>	53	15	C <sub>4</sub> H <sub>5</sub>
105	34	C <sub>8</sub> H <sub>9</sub>	52	13	C <sub>4</sub> H <sub>4</sub>
94	30	C <sub>7</sub> H <sub>10</sub>	51	17	C <sub>4</sub> H <sub>3</sub>
93	100	C <sub>7</sub> H <sub>9</sub>	50	9	C <sub>4</sub> H <sub>2</sub>
92	32	C <sub>7</sub> H <sub>8</sub>	45	11	C <sub>3</sub> H <sub>9</sub>
91	72	C <sub>7</sub> H <sub>7</sub>	41	17	C <sub>3</sub> H <sub>5</sub>
79	15	C <sub>6</sub> H <sub>7</sub>	40	11	C <sub>3</sub> H <sub>4</sub>
77	30	C <sub>6</sub> H <sub>5</sub>	39	34	C <sub>3</sub> H <sub>3</sub>

TABLE I, continued

## 1,5-DIMETHYL-1,4-CYCLOHEXADIENE

m/e	Abundance	Ion	m/e	Abundance	Ion
108	7	$C_8H_{12}$	50	21	$C_4H_2$
93	21	$C_7H_9$	45	17	$C_3H_9$
91	24	$C_7H_7$	44	11	$C_3H_8$
79	8	$C_6H_7$	43	7	$C_3H_7$
77	32	$C_6H_5$	42	6	$C_3H_6$
65	19	$C_5H_5$	41	57	$C_3H_5$
63	11	$C_5H_3$	40	100	$C_3H_4$
53	23	$C_4H_5$	39	46	$C_3H_3$
52	18	$C_4H_4$	38	27	$C_3H_2$
51	46	$C_4H_3$			

molecular weight for these compounds. In the mass spectra of both molecules a prominent fragment ion at a  $m/e$  value of 93, the base peak for 1,2-dimethyl-1,4-cyclohexadiene, is attributed to the loss of a methyl radical from the molecular ion which further confirms these molecules' structure. The fragmentation of the  $m/e$  peak of 93 in 1,5-dimethyl-1,4-cyclohexadiene by a reverse Diels-Alder mechanism<sup>5</sup> produces the base peak of 40 in its mass spectrum:



This fragmentation process is quite common for cyclic unsaturated hydrocarbons.

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## CHAPTER III

### RESULTS AND DISCUSSION

#### Introduction

Vacuum ultraviolet spectral studies of larger molecules have been aided by investigating series of similar compounds relating the spectral variations to corresponding changes in the bonding and structure of the compounds. These larger molecules are expected to have high densities of excited states resulting in absorptions being diffuse. This report contains the results of an investigation for a series of similar compounds wherein the basic molecular framework is the cyclohexane ring system. The investigation focuses on the electronic spectral variations of a six carbon ring system with methyl substituted analogs. It was necessary to elucidate the absorptions associated with the saturated and unsaturated species; therefore, the initial spectra of interest was that of cyclohexane followed by a series of unsaturated cyclohexenes and methyl substituted cyclohexenes. For certain large molecules the spectra contained sharp, atomic-like absorption characteristics of Rydberg absorptions permitting spectroscopic ionization potentials to be determined.

#### Experimental

The spectra reported were obtained with a McPherson one-meter monochromator, model 225, with double beam facilities

having resolution capabilities of  $8.3 \text{ \AA}/\text{mm}$ . The details of the sample cell and specifics of the instrumentation have been described previously.<sup>1</sup> The samples of cyclohexane, cyclohexene, 1,4-cyclohexadiene, 1-methyl-1,4-cyclohexadiene and isotetralin were obtained from Peninsular Chemresearch. The samples of 1,2-dimethyl-1,4-cyclohexadiene and 1,4-dimethyl-1,4-cyclohexadiene were prepared by the Birch reduction of ortho- and meta- xylene.<sup>2</sup> The reduced compounds' structure and molecular weights were confirmed by proton nmr and mass spectral data. Before the spectrum was obtained, each sample was vacuum distilled several times until a sharp melt was obtained.

## Spectra

### Cyclohexane

The lowest energy electronic absorption of this molecule (Figure 1) begins at about  $1650 \text{ \AA}$  and extends to about  $1400 \text{ \AA}$  ( $\lambda_{\text{max}} = 1450 \text{ \AA}$ ,  $\epsilon = 11,500 \text{ l/mol cm}$ ). Adjoining this broad diffuse band is another broad absorption but having several sharp, superimposed bands. Many of these sharp bands have been fit to the Rydberg expression,<sup>3</sup>  $\nu_n = \text{IP} - R/(n-\delta)^2$ . The results of the best fit compared with the corresponding experimental values are given in Table I. This spectrum, having been reported previously by Raymonda and Simpson<sup>4</sup> in a study of a series of alkanes, is included here only for comparison purposes and to indicate the Rydberg series members.



Figure 1. Vacuum Ultra Violet Spectra of Cyclohexane

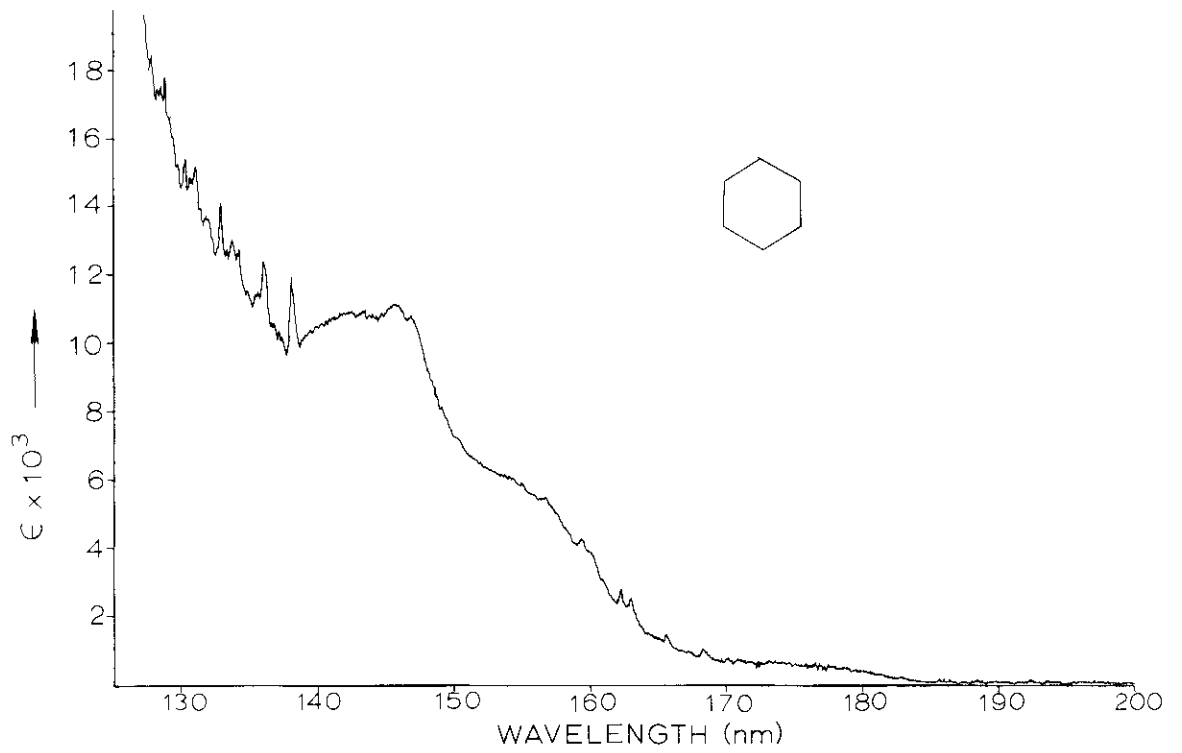


TABLE 2

## RYDBERG SERIES FIT FOR CYCLOHEXANE

<u>n</u>	<u><math>\bar{u}_{obs}</math></u>	<u><math>\bar{u}_{calc}</math></u>	<u><math>\bar{u}_{obs} - \bar{u}_{calc}</math></u>
3	-	66,025	-
4	72,333	72,330	- 3
5	75,160	75,127	-33
6	76,628	76,610	-18
7	77,489	77,491	+ 1
8	78,064	78,056	- 8
$\infty$	-	79,825	-

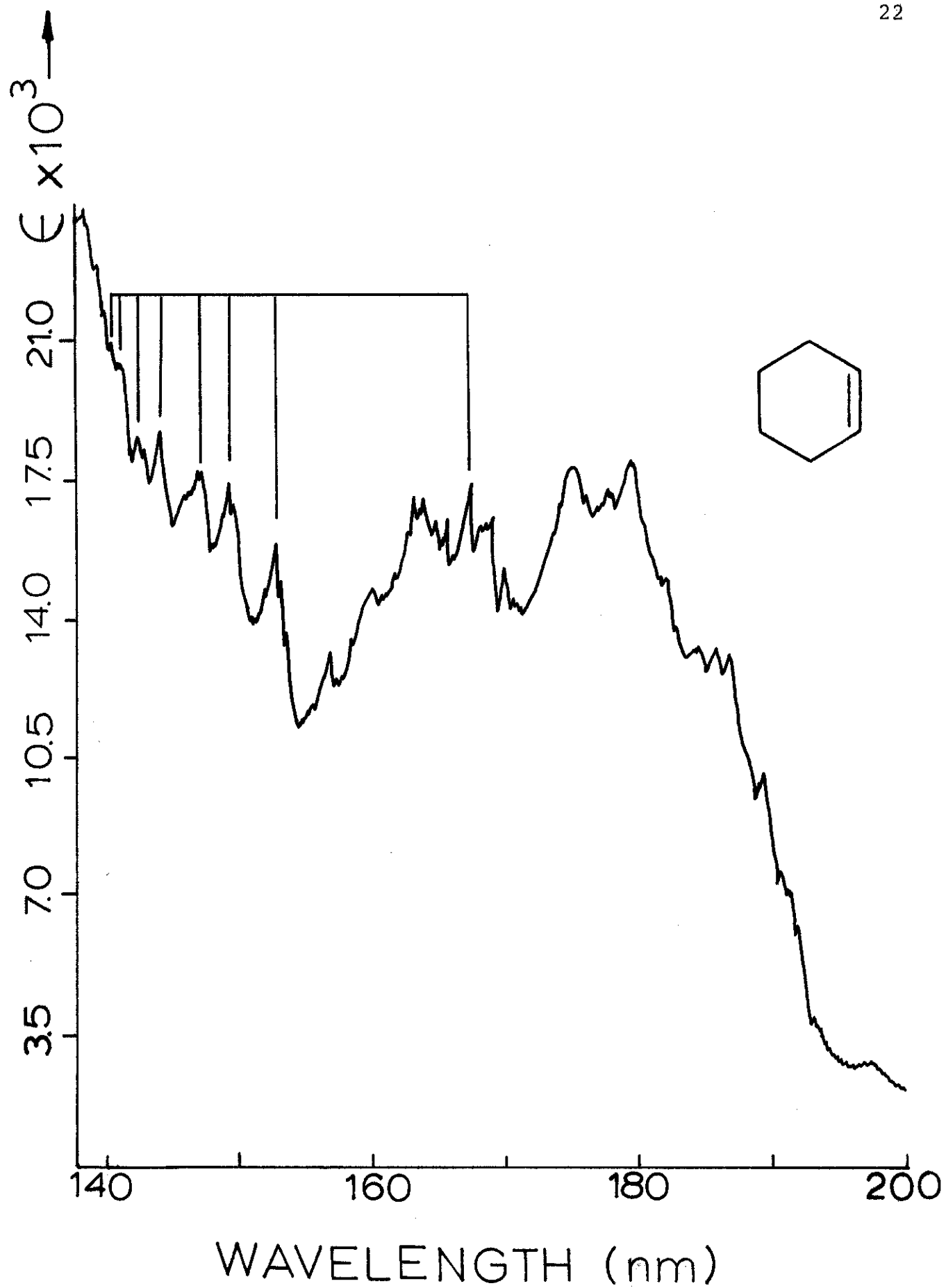
As noted by Raymonda and Simpson, the spectrum (with the exception of the sharp absorptions assigned as Rydbergs) is analogous to that of other alkanes, that being broad absorptions located principally in the higher energy region. The unique feature of this spectrum is the presence of sharp absorptions for this large saturated molecule, meaning that electronic transitions must originate from a sigma orbital. For this Rydberg series calculated, the initial member  $n=3$  is not observed, which is not too unusual for the uniqueness of the origin of the transitions coupled together with the size of the molecule compared to the Rydberg orbital. This variation has been considered by Mulliken<sup>5</sup> to account for variations of compounds containing a single double bond, and will be given in the next section. The high density of excited states for such molecules containing a large number of atoms could have states interacting sufficiently to result in smearing of intensity producing the broad absorptions.

### Cyclohexene

In the vacuum ultraviolet absorption spectra (Figure 2) the dominant feature is the presence of broad diffuse absorptions centered at  $1775 \overset{\circ}{\text{Å}}$  ( $\epsilon = 14,000 \text{ l/mol cm}$ ) and  $1650 \overset{\circ}{\text{Å}}$  ( $\epsilon = 14,000 \text{ l/mol cm}$ ). The next higher energy absorptions occur in the  $1400$  to  $1550 \overset{\circ}{\text{Å}}$  region, where a series of sharper absorptions is superimposed on a broad structureless absorption.

The  $1775 \overset{\circ}{\text{Å}}$  absorption has been observed previously and assigned to the  $V+N (\pi^* \leftarrow \pi)$  transition.<sup>6</sup> The promotion of an

Figure 2. Vacuum Ultra Violet Spectra of Cyclohexene



electron from the relatively destabilized  $\pi$  orbital to the  $\pi^*$  orbital is consistent with the valency excitations for compounds containing a single double bond. A weak absorption shoulder to the longer wavelength side of the intense absorption occurs at  $48,000 \text{ cm}^{-1}$ . The assignment of this weaker absorption as a Rydberg excitation has been determined by Evans by using pressure effects of nitrogen on the vapor phase spectra of cyclohexene.<sup>7</sup> In agreement with Mulliken and Watson,<sup>8</sup> several vibrational members were observed with a  $1360 \text{ cm}^{-1}$  separation, which has been assigned to the C=C stretching frequency of the excited state.

For the higher energy sharper absorptions in the 1400 to  $1550 \text{ \AA}$  region, a Rydberg series has been fit to many of the absorptions with a quantum defect value of 1.05. This value is characteristic of a 's' type Rydberg series<sup>9</sup> and the specific members observed and calculated are given in Table 2. A necessary comment for this data is concerned with the initial Rydberg member ( $n=3$ ). The calculated and observed values differ by about  $5,000 \text{ cm}^{-1}$ , which is greater than expected. Mulliken has discussed variances of this magnitude for initial members of Rydberg series for other compounds containing a single double bond.<sup>5</sup> The difference is attributed to the interaction of the Rydberg orbital with the molecular core. The magnitude of this interaction is dependent on the size of the Rydberg orbital and the size of the molecular valence orbitals. For example, Mulliken calculated the radius of the

TABLE I

## RYDBERG SERIES FIT FOR CYCLOHEXENE

<u>n</u>	<u><math>\bar{u}_{\text{obs}}</math></u>	<u><math>\bar{u}_{\text{calc}}</math></u>	<u><math>\bar{u}_{\text{obs}} - \bar{u}_{\text{calc}}</math></u>
4	59,534	59,565	-31
5	65,202	65,141	+61
6	67,719	67,696	+23
7	69,075	69,075	0
8	69,920	69,903	+17
9	70,437	70,438	- 1
10	70,786	70,805	-19
$\infty$	-	72,175	-



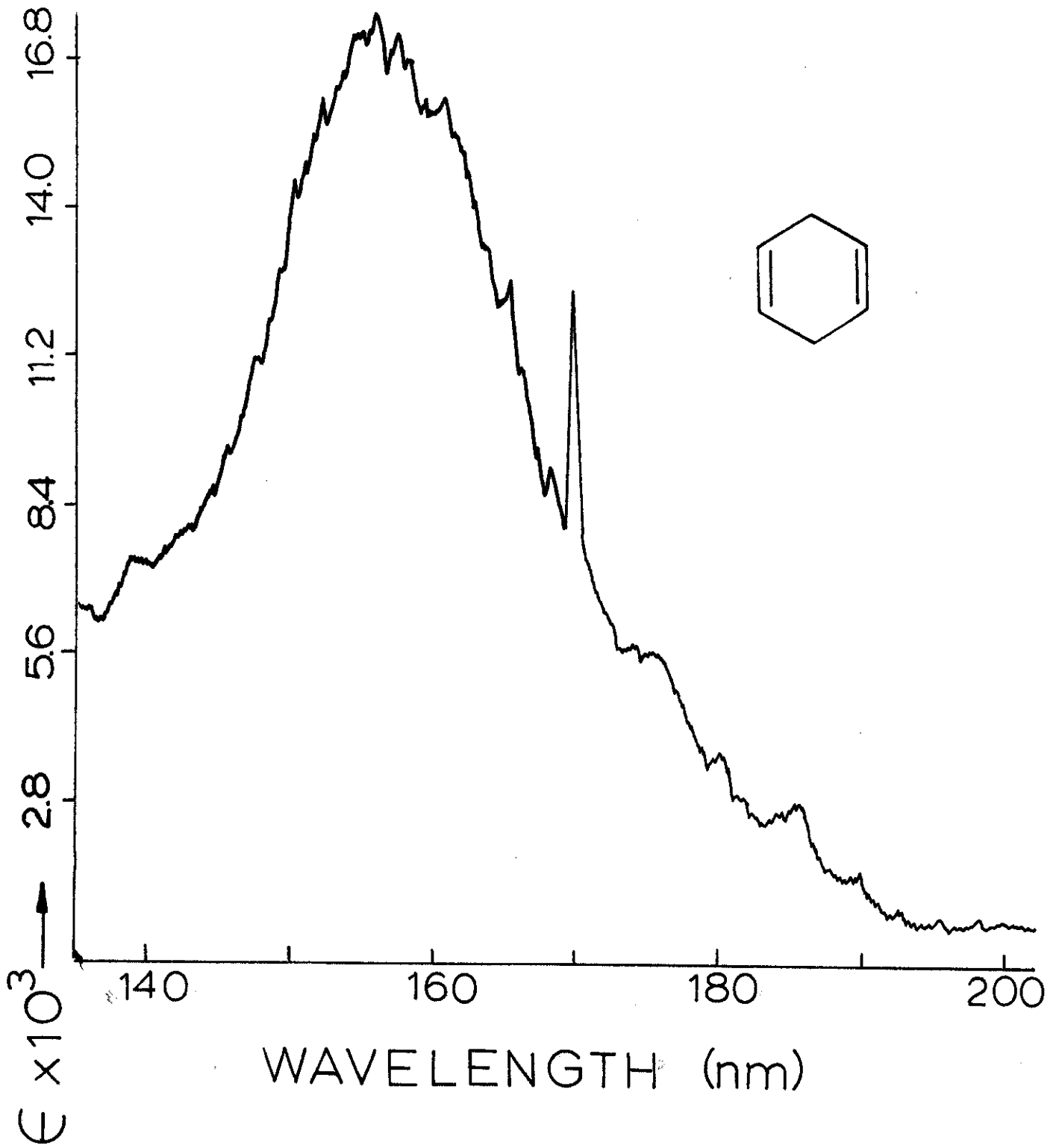
$n=3$  Rydberg orbital of ethylene to be about  $3 \text{ \AA}$ . On this basis it is not unreasonable for this difference to be large for the much larger molecule cyclohexene (ca.  $5,000 \text{ cm}^{-1}$ ).

The adiabatic ionization potential determined by the Rydberg fitting process, containing seven members, is  $8.949^{\pm .005} \text{ ev}$ , which compares favorably with the value reported by Demeo and El-Sayed from photoelectron data.<sup>10</sup> In the photoelectron spectrum reported by Heilbronner the peak corresponding to the vertical ionization potential is shown clearly and has a value of  $9.12 \text{ ev}$ .<sup>11</sup> Using the term value relationship for the different types of molecular Rydbergs as stated by Robin,<sup>9</sup> this Rydberg series would be designated as an 's' type series, as its  $n=3$  member has a term value of  $27,000 \text{ cm}^{-1}$ . Another quantity characteristic of the type of Rydberg series is the quantum defect value,  $\delta$ . The quantum defect value for this series is  $1.05$ , which compares favorably with 's' type Rydberg series for similar compounds: ethylene ( $1.00$ ),<sup>12</sup> propylene ( $.85$ ),<sup>13</sup> cis-2butene ( $1.03$ ),<sup>14</sup> and trans-2-butene ( $.88$ ).<sup>14</sup> By analogy to the previous work on the similar compounds it is concluded that the electron originates from the  $\pi$  orbital, as expected.

#### 1,4-Cyclohexadiene

The absorption spectrum of 1,4-cyclohexadiene (Figure 3) is characterized by the presence of a broad and very intense absorption centered at  $1560 \text{ \AA}$  ( $\epsilon = 17,000 \text{ l/mol cm}$ ). This absorption has some weak absorptions superimposed, the most

Figure 3. Absorption Spectrum of 1,4-Cyclohexadiene



noticeable being the very sharp band at 1698 Å. This sharp band is somewhat unusual as it is the only sharp absorption, and if it is a member of a Rydberg series (as suggested by its shape and location), other similarly sharp absorptions would be expected for the higher energy members. Using the ionization potential reported by Dimeo<sup>10</sup> of 8.82 eV and assuming that this sharp absorption is the n=4 member of a Rydberg series, other weaker absorptions could be located and fitted as additional members to a Rydberg series. The reason that the n=4 member is so much sharper is not known with certainty. Because the density of excited states must be rather large in this specific energy region, the other possible Rydberg members superimposed on the very broad and intense absorption permit greater interaction than for the proposed n=4 member. Therefore, a smearing-out of intensity is expected. This Rydberg series has a quantum defect value of .99, which is consistent with the values of Rydberg series obtained for cyclohexene ( $\delta = 1.05$ ) and other double-bond-containing molecules mentioned.<sup>12-14</sup>

#### 1-Methylcyclohexene and 1,2-Dimethylcyclohexene

Carr and Stucklen observed that the  $\lambda_{\max}$  for the  $\pi^* \leftarrow \pi$  transition in olefins was progressively shifted to longer wavelengths as each hydrogen on ethylene was substituted with an alkyl group.<sup>15</sup> This shift was related to the number of alkyl groups substituted on ethylene and not to the type of the alkyl substituent. The same trend is observed with 1-methylcyclohexene and 1,2-dimethylcyclohexene when compared to cyclohexene.

In the absorption spectra (Figure 4) of these methyl substituted cyclohexenes, it is observed that the  $\lambda_{\max}$  for the  $\pi^* \leftarrow \pi$  transition 1-methylcyclohexene is shifted to 1810 Å as compared to 1775 Å for cyclohexene. An even larger shift is predicted when an additional methyl group is added to this molecule to give 1,2-dimethylcyclohexene. This is readily borne out in its electronic spectrum, in which the  $\lambda_{\max}$  for the  $\pi^* \leftarrow \pi$  absorption wavelength is located at 1890 Å.

The assigned  $\pi^* \leftarrow \pi$  absorption band in both molecules is characterized by a number of vibrational spacings. Selection rules would predict that 1,2-dimethylcyclohexene would have fewer vibrations excited than 1-methylcyclohexene due to its higher degree of symmetry. The spectra agree with this prediction. The average vibrational frequency for 1-methylcyclohexene in the region from 1890 Å to 1745 Å is  $1500 \text{ cm}^{-1}$ . For 1,2-dimethylcyclohexene the excited state vibrational spacing is  $1425 \text{ cm}^{-1}$  in the region 1990 Å to 1750 Å. These vibrational separation energies can be compared with the  $1400 \text{ cm}^{-1}$  spacing reported for both trimethylethylene and tetramethylethylene, which are contained as moieties within 1-methylcyclohexene and 1,2-dimethylcyclohexene, respectively.<sup>16</sup>

1-Methyl-, 1,2-Dimethyl-, and 1,5-Dimethyl- 1,4-Cyclohexadiene

When compared to the absorption spectra of the cyclohexenes, the electronic spectra of 1-methyl-, 1,2-dimethyl- and 1,5-dimethyl- 1,4-cyclohexadiene (Figure 5) in the vacuum ultraviolet

Figure 4. Absorption Spectra of 1-Methylcyclohexene  
and 1,2-Dimethylcyclohexene

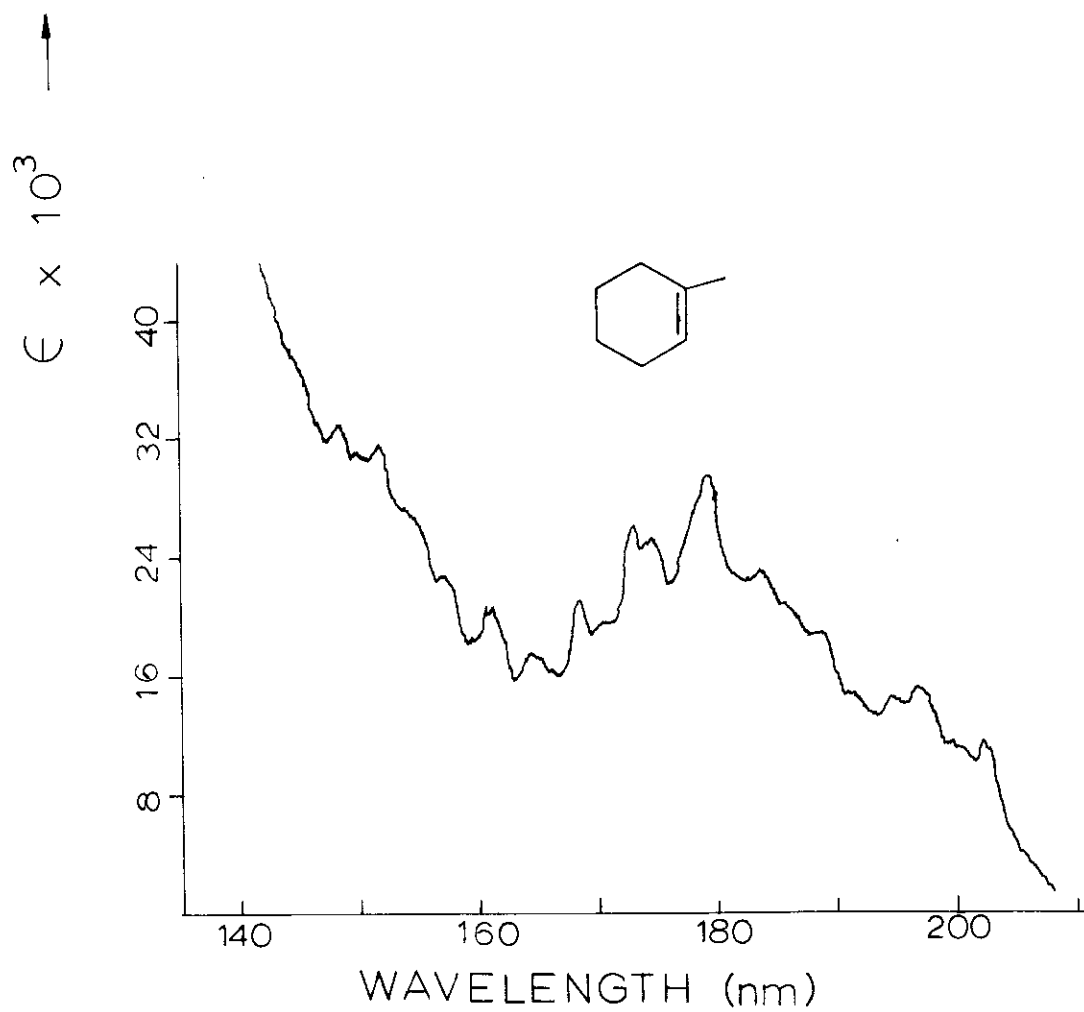
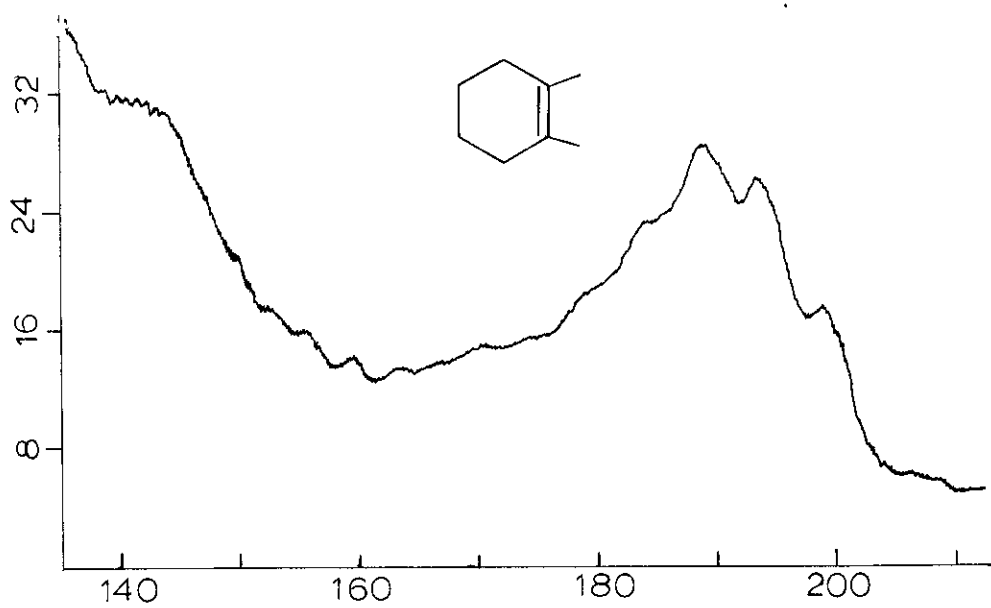
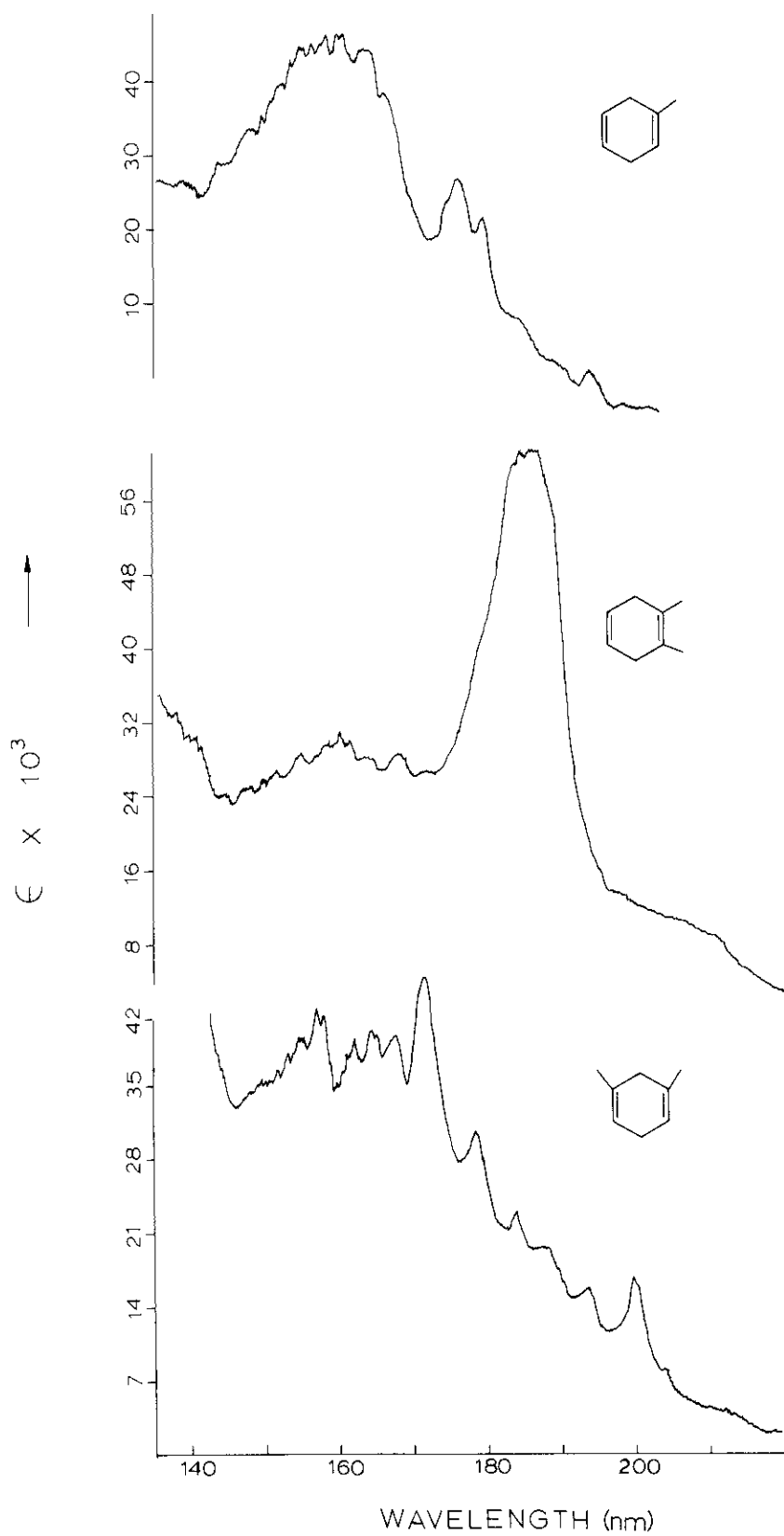


Figure 5. Vacuum Ultra Violet Spectra of 1-Methyl-,  
1-2-Dimethyl-, and 1,5-Dimethyl- 1,4-Cyclohexadiene





indeed becomes more complex. The spectrum of 1-methyl-1,4-cyclohexadiene is quite similar to that of 1,4-cyclohexadiene with a diffuse broad band located at  $1600 \text{ \AA}$  assigned to the  $\pi^* \leftarrow \pi$  excitation. Vibrational spacings on this band are apparent but no consistent separation energy could be determined. A distinct shoulder is located on this broad absorption at  $1760 \text{ \AA}$ , with an onset of other weak vibrational bands beginning at  $2000 \text{ \AA}$ . Possibly several vibrational modes are occurring which make vibrational patterns difficult to ascertain.

The spectrum of 1,5-dimethyl-1,4-cyclohexadiene also has semblance with that of 1,4-cyclohexadiene. The center of the very broad absorption band assigned as a  $\pi^* \leftarrow \pi$  is located at  $1675 \text{ \AA}$ , with a large 'step-out' of absorption to the  $2200 \text{ \AA}$  region. A fairly sharp absorption comparable with the  $1698 \text{ \AA}$  band of 1,4-cyclohexadiene in energy has a wavelength of  $1710 \text{ \AA}$ . However, this band is not believed to be a Rydberg band as the comparable band in 1,4-cyclohexadiene's spectrum is believed to be. Using high pressure techniques of an inert gas in the sample cell would readily discern whether either of these two absorptions is Rydberg in character.<sup>7</sup> Some regular vibrational spacing in the  $1790\text{-}2000 \text{ \AA}$  region is observed, with an average vibrational peak-to-peak value of  $1490 \text{ cm}^{-1}$ . This vibrational spacing is consistent with other assigned, excited-state C=C stretching frequencies.

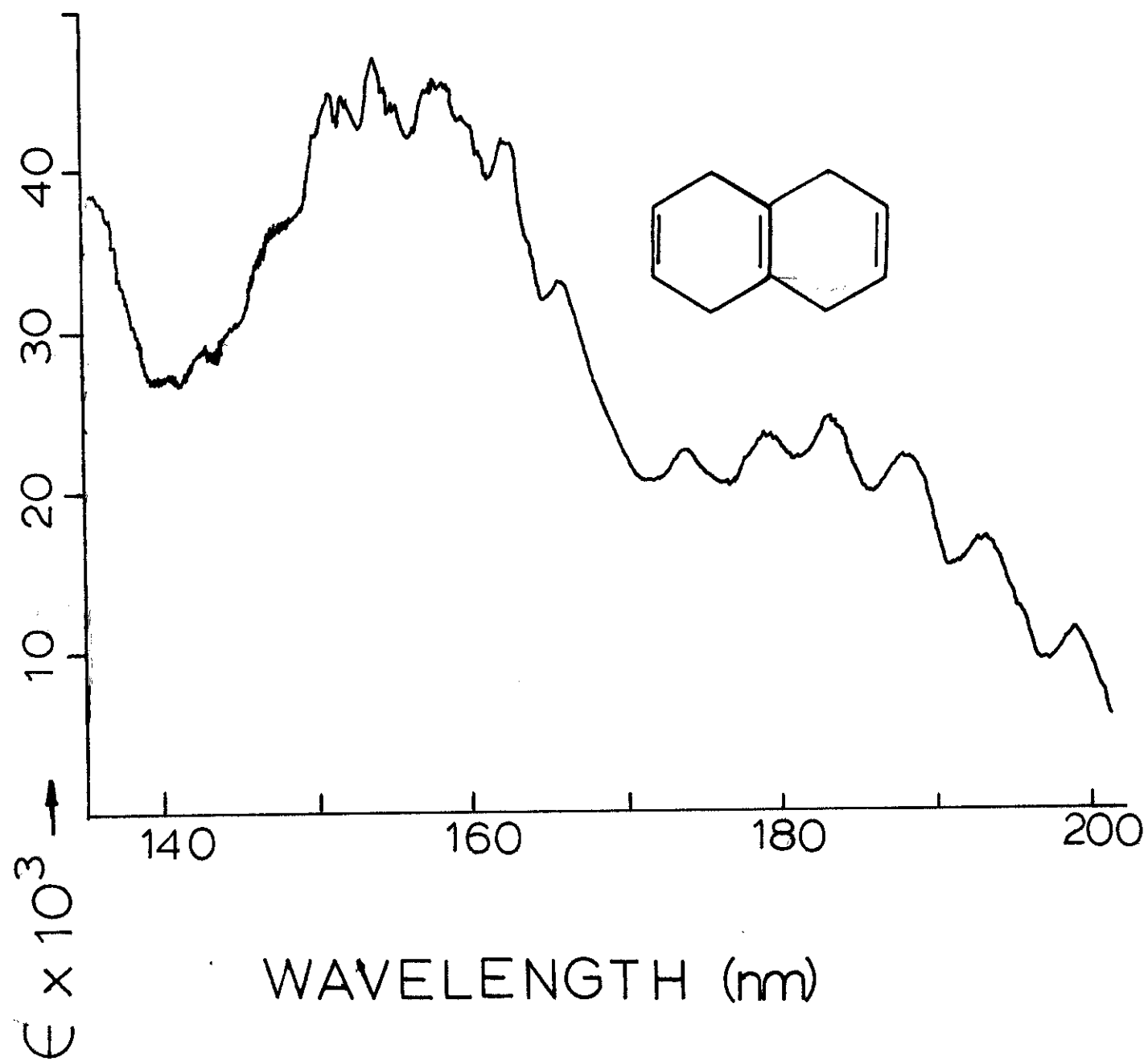
The spectrum of 1,2-dimethyl-1,4-cyclohexadiene is unlike the spectra of other substituted 1,4-cyclohexadienes. The

dominating feature of its spectrum is a somewhat broad, intense band centered at  $1860 \text{ \AA}$ . This is close to the energy of the  $\pi^* \leftarrow \pi$  assigned to 1-methylcyclohexene, but of much higher intensity ( $\epsilon \sim 20,000 \text{ l/mol cm}$ ). A much broader absorption at a shorter wavelength is centered about  $1600 \text{ \AA}$ . The vibrational spacing for this band is approximately  $1250 \text{ cm}^{-1}$ , which is on the low end for a vibration involving a C=C stretch in the excited state. However, this band is still assigned as a second  $\pi^* \leftarrow \pi$  transition. Attempts to explain this molecule's absorption profile are discussed in a later section.

#### Isotetralin

In a continuation of studying nonconjugated, olefinic molecular systems the absorptions spectrum of isotetralin was also investigated. The vacuum ultraviolet spectra (Figure 6) of this compound also has similarity with the spectra of 1,4-cyclohexadiene in that it contains a broad, somewhat diffuse band centered about  $1570 \text{ \AA}$ . Some vibrational members are noted as in 1,4-cyclohexadiene, but no regular vibrational spacing can be determined. An additional feature of this spectrum, however, is a lower intense band centered about  $1850 \text{ \AA}^{17}$  but dominated by a well-spaced, vibrational separation of  $1440 \text{ cm}^{-1}$ . Both of these bands in the isotetralin spectrum are assigned as two different  $\pi^* \leftarrow \pi$  excitations. The unique feature of this molecule is that it contains three parallel, nonconjugated bonds, providing an interesting theoretical model which will be discussed in a later section.

Figure 6. Vacuum Ultraviolet Spectra of Isotetralin



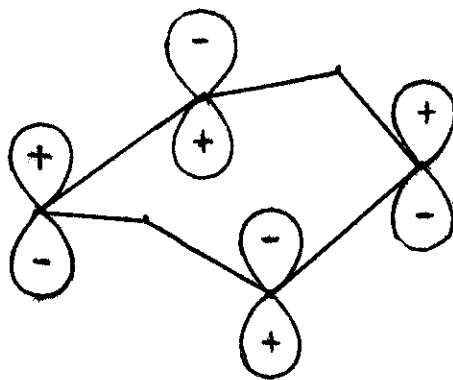
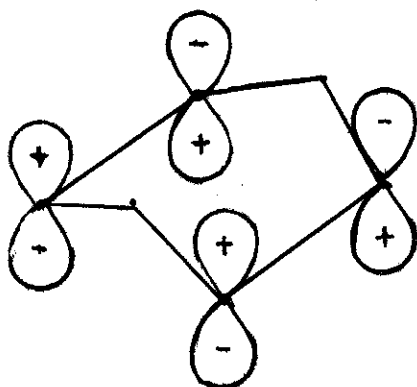
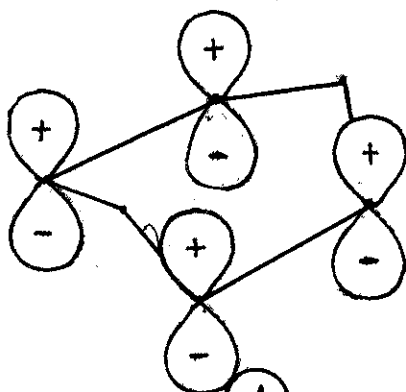
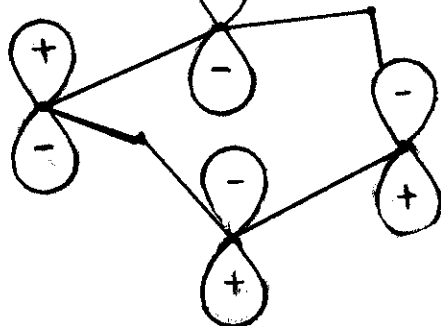
### Theoretical Aspects

In addition to the spectroscopic ionization potential, these spectra provide data necessary to determine the interactions occurring between independent  $\pi$  orbitals within a single molecule. The molecular spectra contained in this report are for compounds with localized  $\pi$  orbitals, non-conjugated olefins. The interactions of non-conjugated  $\pi$  bond systems have been the subject of various molecular orbital calculations, including Huckel,<sup>18</sup> Pariser and Parr,<sup>19</sup> extended Huckel,<sup>20</sup> and MINDO approximations.<sup>21</sup> Another theoretical model, Independent Systems,<sup>22</sup> has been used to describe the electronic spectral profile for several allenic compounds, also containing non-conjugated  $\pi$  bonds. Therefore, one of the objectives of this study is to determine the validity of the theoretical models for describing the interactions of these molecular systems.

#### Molecular Orbital Calculations

The compound 1,4-cyclohexadiene contains two  $\pi$  bonds in the same basic structural framework as cyclohexene such that the two  $\pi$  bonds are parallel and non-conjugated. These two  $\pi$  systems will interact, shifting the energetics of the two  $\pi$  orbitals. The results of MINDO calculations for 1,4-cyclohexadiene predict the splitting to be 1.01 eV.<sup>21</sup> Similar calculations within the CNDO/2 approximations<sup>23</sup> predict a similar splitting (3eV) between the  $\pi$  and  $\pi^*$  orbitals. The basis set of four p-orbitals results in four molecular orbitals, two bonding  $\pi$  orbitals, and two antibonding  $\pi^*$  orbitals, as shown in Figure 7,

Figure 7.  $\pi$  and  $\pi^*$  Orbitals for 1,4-Cyclohexadiene


 $a_2$  —

 $b_2$  —

 $a_1$   $\uparrow\downarrow$ 

 $b_1$   $\uparrow\downarrow$ 
 $E$   $\uparrow$



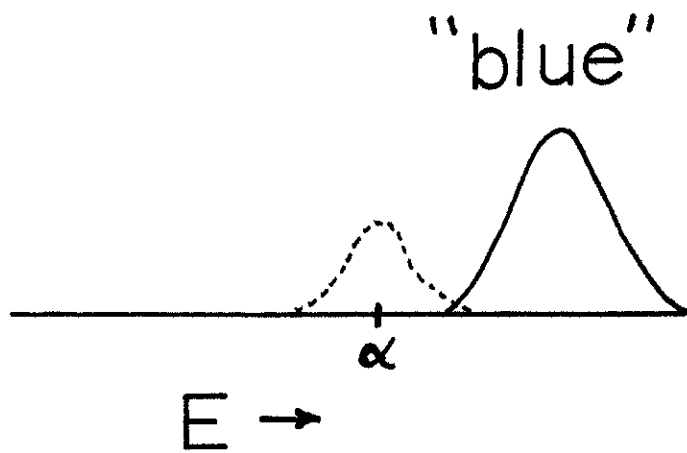
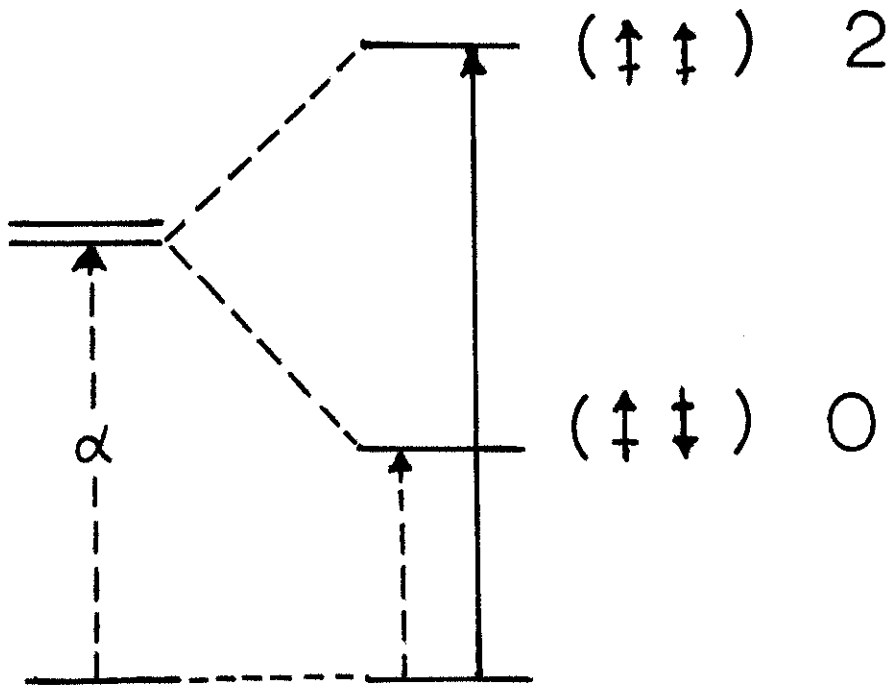
where each is labeled according to its symmetries in terms of a linear combination of the basis set p-orbitals. In addition to the p-orbitals, hydrogenic s orbitals representing the methylene's interaction are also given. Even though the Highest Occupied Molecular Orbital (HOMO), which has  $a_1$  symmetry, is the most symmetric, it is not predicted by CNDO/2 results to be the most stable of the two occupied molecular orbitals. This result has been reasoned by Hoffmann<sup>20</sup> in that the two orbitals of the same symmetry, the methylene group orbitals and the  $a_1$  molecular orbital, interact to a sufficient degree so that the totally symmetric  $\pi(a_1)$  orbital is pushed above the less symmetric  $\pi(b_1)$  orbital in energy.

#### Independent Systems

Consider the polarization of the  $\pi^* \leftarrow \pi$  transition in cyclohexene. If one uses a transition dipole orientation as designated for ethylene,<sup>22</sup> then the transition moment for cyclohexene would be polarized along the olefin moiety. If cyclohexene is made further unsaturated to give 1,4-cyclohexadiene, then a dipole-dipole interaction could be used for this system to describe the new  $\pi^* \leftarrow \pi$  transition energies and their intensities. A diagram representing this interaction is shown in Figure 8. Upon interaction of the individual transition dipole, two new excitation energies are present which are separated by twice the interaction energy  $\beta$ . Approximating the intensities of the transition by vector addition, the upper energy transition is expected

Figure 8. Interaction Diagram for Parallel Transition  
Dipoles

Transverse ( $\theta = 90^\circ$ )



to contain twice the intensity of the  $\pi^* \leftarrow \pi$  and to be shifted to higher energy. In addition, the lower energy transition is predicted to have zero intensity. For 1,4-cyclohexadiene there is observed a  $\lambda_{\max}$  at  $63,700 \text{ cm}^{-1}$ , with an oscillator strength of .71 assigned to the  $\pi^* \leftarrow \pi$ . There is now lower energy band of significant intensity.

Increased alkyl substitution on olefins is known to cause a shift to lower energies in the  $\pi^* \leftarrow \pi$  excitation.<sup>15</sup> This is observed in the spectra of cyclohexene methyl substituted at the 1-position. The  $\lambda_{\max}$  for the  $\pi^* \leftarrow \pi$  transition in 1-methylcyclohexene is observed at  $55,000 \text{ cm}^{-1}$ , with an oscillator strength of  $.25 \pm .05$ . Just as in 1,4-cyclohexadiene, the transition dipole model for 1,5-dimethyl-1,4-cyclohexadiene (see spectra Figure 3) predicts the  $\pi^* \leftarrow \pi$  energy to be shifted to the higher energy side of the  $\pi^* \leftarrow \pi$  in 1-methylcyclohexene, with approximately twice the intensity. The  $\pi^* \leftarrow \pi$  band for this molecule is a broad maximum located at  $60,600 \text{ cm}^{-1}$ , with a total oscillator strength of  $.58 \pm .05$ .

The model used in making qualitative predictions is primitive but the trends predicted do agree with experimental data. Simpson has developed a more refined theory concerning transition dipoles and their interactions with a view of Independent Systems analysis.<sup>22</sup> It has been applied to a series of alkanes<sup>4</sup> and methyl-substituted allenes<sup>24</sup> with reasonable success. This more quantitative description requires knowledge of the chromophore's energy of interest ( $\alpha$ 's), interaction energies ( $\beta$ 's),

and the transition energies after interaction (E's). When applied to other methyl substituted 1,4-cyclohexadienes, the transition dipoles are assumed to be similarly oriented along the axis of the carbon-carbon double bond and parallel to one another.

The interaction energy,  $\beta$ , for these transition dipoles is derived to be

$$\beta \propto 2/M - 2/N$$

$$M = \frac{R}{\tan^{-1} \left( \frac{v_a/2 - v_b/2}{R} \right)}$$

$$N = \left\{ (v_a/2 + v_b/2)^2 + R^2 \right\}^{1/2}$$

The magnitude of interaction is dependent upon the distance separating the two dipoles, their lengths, and natural non-interacting energies. The interaction matrix for parallel transition dipoles in 1,4-cyclohexadiene is given as

$$\begin{bmatrix} \alpha_1 - E & \beta \\ \beta & \alpha_2 - E \end{bmatrix}$$

The solution of this matrix readily bears out the empirical observation that the upper transition energy corresponding to the in-phase orientation of the transition dipole ( $\uparrow\uparrow$ ) contains more intensity than the out-of phase orientation ( $\uparrow\downarrow$ ). The energies predicted for the two combinations (the non-interacting transition manifolds) are

$$E = \{ \alpha_1 + \alpha_2 \pm [(\alpha_1 - \alpha_2)^2 + 4\beta^2]^{1/2} \} / 2$$

where  $\alpha_1$  and  $\alpha_2$  are the oscillator strengths, transition dipole lengths, and the band maxima of the  $\pi^* \leftarrow \pi$  transition(s) for a

series of cyclohexenes, 1,4-cyclohexadienes observed in the vacuum ultraviolet (VUV) spectral region (see Table 3). Substituting the transition moment lengths obtained from the spectra for cyclohexene ( $\mu_{CH}$ ) and 1-methylcyclohexene ( $\mu_{MCH}$ ) into equation (1), a value for  $\beta$  is obtained for 1-methyl-1,4-cyclohexadiene whose spectrum is given in Figure 5. Using the observed transition energies for the  $\pi^* \leftarrow \pi$  for this molecule, 1,4-cyclohexadiene, and 1,5-dimethyl-1,4-cyclohexadiene, two forms of equation (2) are derived. Matching these two equations with the  $\beta$  value from equation (1), values for  $\alpha_1$ ,  $\alpha_2$ , and  $\beta$  are calculated and substituted into the interaction matrix, giving the following eigenvectors:

$$\mu_1 = .884 \mu_{CH} - .456 \mu_{MCH} = .32$$








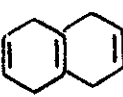
$$\mu_2 = .527 \mu_{CH} + .85 \mu_{MCH} = .92$$

Using these transition moment lengths, the oscillator strengths are calculated, the intensity for the lower energy absorption being predicted to be approximately one-third of the value observed. This difference is attributed to a coupling of this transition with a totally symmetric vibration which could account for the increase the observed intensity.

Similar calculations were made for 1,2-dimethyl-1,4-cyclohexadiene. The parameters used in deriving a value for  $\beta$  are transition moment lengths for the  $\pi^* \leftarrow \pi$  in 1-methylcyclohexene and 1,2-dimethylcyclohexene. To obtain two forms of equation (2), knowledge of the  $\pi^* \leftarrow \pi$  band maxima of 1,4-cyclohexadiene and 1,2,4,5-tetramethyl-1,4-cyclohexadiene is required. The VUV spectra for the latter was not obtained, as attempts to synthesize

TABLE III

## OSCILLATOR STRENGTHS

	$\underline{f}$	$\lambda_{\text{max}}$	$\underline{\mu}$
	.31	56,300	.70
	.25	55,250	.65
	.71	63,700	1.01
	.58	60,600	.94
	.23	52,900	.63
	.23	57,150	.61
	.61	62,500	.95
	.48	54,000	.84
	.52	62,500	.87
	.38	54,600	.80
	.84	64,100	1.10

the compound were unsuccessful and no source could be located to purchase the compound. However, since dimethyl substitution of 1,4-cyclohexadiene at the 1 and 5 sites shifted the  $\pi^* \leftarrow \pi$  max  $3,000 \text{ cm}^{-1}$  to lower energy, tetramethyl substitution at the 1,2,4,5 sites was assumed to shift the band maxima  $6,000 \text{ cm}^{-1}$  to lower energy. Making this assumption, the  $\alpha$  and  $\beta$  terms were calculated and inserted into the interaction matrix along with the observed  $\lambda_{\text{max}}$  values for 1,2-dimethyl-1,4-cyclohexadiene. The resultant characteristic equations are

$$\mu_1 = .31\mu_{\text{DMCH}} + .95\mu_{\text{CH}} = .31(.63) + .95(.70) = .87$$

$$\mu_2 = .95\mu_{\text{DMCH}} - .31\mu_{\text{CH}} = .95(.63) - .31(.70) = .38$$

The theoretical value for the lower-intensity, lower-energy band varies markedly from the experimental value in Table 3, but that for the high intensity band is predicted closely. However, the 'independence' of the  $\pi^* \leftarrow \pi$  transitions in this molecule is questionable, due to the large inductive effect of the two methyl groups on one olefin moiety. This may effect a delocalization mechanism through the methylene groups within the ring, affecting the model used for these calculations.

To test the Independent Systems model further, it was decided to take all the parameters derived thus far and 'build' the intensity profile for a molecule not investigated in the VUV. The molecule investigated was isotetralin. This molecule contains three parallel non-conjugated olefin groups, yet close enough for interaction. The operating parameters for the interaction matrix were chosen as follows: (1) the  $\alpha$  and  $\beta$  values



for the centred olefin group was assumed to be equivalent to that for the disubstituted olefin group in 1,2-dimethyl-1,4-cyclohexadiene; (2) the interaction energy between olefins one and three was one-eighth the value for 1,4-cyclohexadiene, and (3) the natural frequencies ( $\alpha$ ) for these latter two groups were chosen as equivalent to those for 1,4-cyclohexadiene. Substituting these values into a three-by-three interaction matrix resulted in a prediction of transition moment lengths of .35 and 1.05 for the low-and high-energy bands, respectively. These can be compared with the observed values .80 and 1.10. A large amount of the intensity for the lower energy band is suggested to occur through strong vibronic coupling. However, in light of the approximations made, the Independent Systems theory seems to work satisfactorily for this system.

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## CHAPTER IV

### CONCLUSIONS

Vacuum ultraviolet (1200-2000 angstroms) spectroscopy is fundamental for studying higher energy  $\sigma^* \leftarrow \sigma$ ,  $\pi^* \leftarrow \pi$ , and Rydberg transitions in molecules. This is particularly true when investigating the electronic energy absorptions of cyclohexane, which has no appreciable absorption until 1600 angstroms. Above this energy its spectra is dominated by two types of absorptions: (1) broad absorption bands largely attributed to  $\sigma^* \leftarrow \sigma$  transitions, and (2) a number of sharp bands assigned as Rydberg transitions. These sharp bands are common for atoms and some simple molecules; however, they are not common for molecules as complex (large) as cyclohexane. This observation is attributed to the high density of bound excited states for molecules. The many atomic centers of molecules affect the Rydberg states by spreading the intensity among several excited states, obscuring the sharp bands into other absorption bands. However, in this case there are enough sharp Rydberg bands present of adequate distinction in cyclohexane's VUV spectrum to fit a first ionization potential of  $9.897 \pm 0.005$  electron volts.

These spectral properties of cyclohexene were investigated relative to the similarities and/or dissimilarities of

cyclohexane. The VUV spectra of cyclohexene contains intensity profiles at energies similar to those observed for both olefinic molecules and cyclohexane. Olefin-containing molecules such as ethylene,<sup>1</sup> propene,<sup>2</sup> cis- and trans- 2-butene<sup>3</sup> have absorption bands that can be fitted to 's' type Rydberg series and are assigned as originating from the  $\pi$  bond of these molecules. The quantum defect numbers for 's' type Rydberg series approximate unity in value and are listed respectively for these olefinic molecules as 1.0, .85, 1.03, and .88. The spectra of cyclohexene also has a series of absorptions which can be fitted to a similar 's' type Rydberg series with a quantum defect value of 1.05. Therefore, it is noted that Rydberg-assigned absorptions are occurring for the olefins mentioned, with moderate variations in the absorption energies depending upon the substituent(s) on the unsaturated carbons. This is supported by the fact that the first ionization potentials of the above-listed olefins range from 9.0 to 10.5 electron volts,<sup>1-3</sup> with the unseated electrons originating from the  $\pi$  bond. The spectrum of cyclohexene also contains a number of broad underlying bands similar to the  $\sigma^* \leftarrow \sigma$ -assigned bands observed in the same spectral region of cyclohexane. Thus the spectrum of cyclohexene is of interest when the olefin moiety is viewed as conferring 'molecule-within-molecule' spectral properties. That is, the spectrum can be roughly viewed as an addition spectrum of cyclohexane and ethylene. However, the Rydberg excitations originating from

the  $\pi$  bond in ethylene are shifted to lower energies when compared with the same excitations in cyclohexene.

The results of semi-empirical molecular orbital calculations were used to aid in the ordering of the  $\pi$  and  $\pi^*$  molecular orbitals for 1,4-cyclohexadiene. These calculations were made to determine the relative magnitude of interaction of the  $\pi$  bonds via indirect interaction through the methylene groups of this molecule and direct interaction (through-space) between the olefinic groups. Allowing only MO's of the same symmetry to interact,<sup>4</sup> these calculations supported the prediction that before interaction the lowest occupied MO would be shifted above the energy of the highest occupied MO after interaction.

When electronic transitions are represented by transition dipoles, then spectral properties of molecules can often be successfully predicted. By treating transitions independently and classically as dipoles, the effect of one transition dipole on another can be determined when their dipole lengths, the orientation of one dipole to another, and their natural frequencies are known.<sup>5</sup> In the Independent Systems analysis of 1,4-cyclohexadiene, 1,2- and 1,5- dimethyl-1,4-cyclohexadiene, and isotetralin, there was general agreement between the intensities calculated and those observed for the higher energy bands. For the lower energy bands inductive effects and vibronic coupling are reasoned as possible mechanisms to account for discrepancies observed between theory and experiment.

However, in each case the trends and general intensity profile for each molecular spectra were in general agreement with those predicted.

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APPENDIX

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## ELECTRONIC STRUCTURE AND BONDING OF ALLYLITHIUM

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### Summary

The results of CNDO/2 calculations have been used to determine the equilibrium geometry for allyllithium which is predicted to be a non-planar "bridge" structure. The lowest energy configuration (LEC) is described in molecular orbital terms which stress the importance of the lithium's position in permitting it to utilize all its valence orbitals in bonding with the allyl moiety. Charge densities, the theoretical dipole moment, and variations of configurations are discussed in relation to the spectroscopic measurements of allyllithium. Utilizing the geometry of the allyllithium monomer (LEC), a proposed dimer configuration is reported which is in feasible agreement with the experimental aggregation properties. The solvent interactions were considered by utilizing two molecules of ammonia as the electron donor with allyllithium. The results of the calculations predict that the solvation of the lithium by ammonia increases the allyllithium fragment separation with concomitant changes in the electron densities and bonding populations.

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### Introduction

Allylic lithium species have been proposed as possible intermediates in anionic polymerization reactions where organolithium reagents have been used as initiators [1]. Therefore, spectroscopic studies, particularly proton magnetic resonance of several molecules containing the allyllithium component have been made to gain a better understanding of the bonding and structure of this important species [2]. This paper is concerned with the results of molecular orbital calculations using the CNDO/2 approximations [3] with particular interest in the predicted properties compared to experimental values. The CNDO/2 method has been quite successful in calculating properties such as bond angles and to lesser degree, bond lengths [4], and will be employed for predicting the lowest energy configuration for the allyllithium molecule. The wave functions calculated by this method will be utilized to describe the bonding and electronic structure.

## Results and discussion

### Equilibrium geometry

The following assumptions were made in the calculations to predict the equilibrium geometry of allyllithium: (1) C—H bond lengths were chosen as 1.09 Å, (2) hydrocarbon bond angles were given values of 109.5 degrees for  $sp^3$  hybridized carbons and (3) 120.0 degrees for the  $sp^2$  terminal carbon. All values in the original CNDO/2 parameterization were left unaltered.

Preliminary calculations were made with a lithium—carbon [5] bond distance of 2.20 Å with the molecule in a propylene configuration; however, changing the hybridization on the saturated carbon from an  $sp^3$  to an  $sp^2$ , with the lithium coordinates unchanged in this configuration, stabilized the molecule. Also, rotation about the carbon—carbon single bond for the propylene model produced the greatest stability when the lithium was on a line perpendicular to the plane defined by the three carbons. Therefore, a point of interest for the ground state is the location of the lithium atom relative to a planar allylic framework which is given in Fig. 1. Movement of the lithium in the C(1)—C(2)  $\pi$  cloud indicated a more stable configuration was obtained with the lithium located above carbon(2). This increased stabilization is the result of increased bonding between the 2s-orbitals of the four atoms and the  $\pi$  bond of the allyl fragment with the  $p_x$  orbital on the lithium atom. Due to the proximity of two partial positive charges,  $Li^+$  and  $C(2)^+$ , increasing the distance separating the two atoms in the yz plane further stabilized the molecule in a symmetric nonplanar bridge structure. The resulting lowest energy configuration (LEC) is given in Fig. 2 as determined by all possible displacements of the lithium and carbon atoms. Any deviation of the allyl fragment from planarity was found to be less stable. A planar configuration with the lithium atom in the plane of the allyl fragment was found less stable than the nonplanar configuration given in Fig. 2. The separations for the LEC are 2.19 and 2.03 Å for Li—C(1) and Li—C(2) which are slightly smaller than the typical values of 2.36 and 2.12 Å calculated for the unsaturated lithium complex, lithium naphthalide [6].

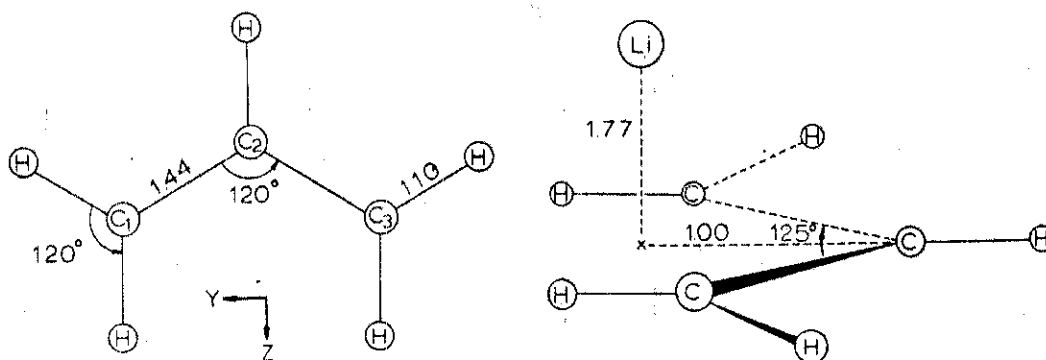


Fig. 1. Geometry of the allylic component for the calculations. All bond angles are 120° and carbon—hydrogen bond distances are the same.

Fig. 2. The predicted geometry for allyllithium, where the lithium atom is located above the plane of the allyl and between the projection of the carbon and hydrogen atoms.

Crystallographic studies have been made by Brooks and Stucky [7] for tetramethylethylenediamine lithium triphenylmethane complex which contains a component analogous to the allyllithium anionic moiety. The portion of the molecular complex analogous to allyllithium is a nonplanar, nonsymmetrical bridge structure with lithium terminal carbon internuclear distances of 2.51 and 2.49 Å and a lithium-carbon(2) distance of 2.23 Å. The geometry predicted for allyllithium is the same as the corresponding component of the complex except for slightly smaller lithium carbon separations and a plane of symmetry for allyllithium. Therefore, the CNDO/2 results are encouraging since the LEC converged on this geometry assuming only the C-H bond distances and the standard hybridized carbon bond angles.

#### Bonding description

Within the CNDO approximations only the valence electrons are considered; thus allyllithium has the nine lowest energy molecular orbitals occupied. The degree of participation of the lithium in each molecular orbital (MO) varies and in certain MO's the contribution is negligible. In Table 1 are given the coefficients (greater than 0.10), not including the hydrogen coefficients. The molecular wavefunctions are numbered according to their increasing eigenvalues [i.e.,  $\psi(1)$  is the most stable MO].  $\psi(1)$  and  $\psi(6)$  are mostly  $\sigma$  bonding MO's between lithium and the three carbons whereas the lithium coefficients in  $\psi(3)$  exhibit a greater degree of bonding with C(2). In  $\psi(2)$  and  $\psi(9)$  the lithium  $p_y$  orbital has overlap values of 0.26 and 0.16 with the terminal carbon  $2s$  and  $2p_x$  orbitals, respectively. Because of the large coefficients of lithium  $p_y$  atomic orbital in  $\psi(2)$  and  $\psi(9)$ , it is of major importance in the overall bonding (see Fig. 3). Evident in these molecular orbitals of allyllithium is the utilization of all low-energy orbitals on lithium to increase its bonding with the allyl moiety. Using Mulliken's population analysis [8], the overlap population values for lithium-C(1) and lithium-C(2) are 0.37 and 0.34 relative to 0.88 and 0.65 for carbon-carbon and C(2)-H(5), respectively. Assuming that the strength of the bond between two atoms varies with the overlap population, the bond strength of the lithium-carbon bonds would be predicted to be about one half that of the carbon-carbon or C(2)-H(5) bonds.

A CNDO/2 calculation was also made for the allyl anion using the same geometry for the hydrocarbon framework as in the LEC of allyllithium. The following was noted in the MO's and their eigenvalues: (1) the relative ordering of the MO's according to their energy values of the allyl anion and allyllithium

TABLE 1

#### SELECTED VALENCE ORBITALS OF ALLYLLITHIUM

$\psi(1) = 0.41s(1) + 0.56s(2) + 0.41s(3) + 0.23s(\text{Li}) - 0.26p_x(\text{Li}) + 0.18p_y(1) - 0.18p_y(3) + 0.14p_z(2)$
$\psi(2) = -0.48s(1) + 0.48s(3) + 0.44p_y(2) + 0.24p_y(\text{Li})$
$\psi(3) = 0.14s(1) - 0.32s(2) + 0.14s(3) + 0.33p_z(1) - 0.45p_z(2) + 0.33p_z(3) + 0.20p_z(\text{Li})$
$\psi(6) = 0.18s(\text{Li}) + 0.51p_x(1) + 0.65p_x(2) + 0.51p_x(3) - 0.11p_z(\text{Li})$
$\psi(9) = -0.54p_x(1) + 0.54p_x(2) + 0.38p_y(\text{Li})$

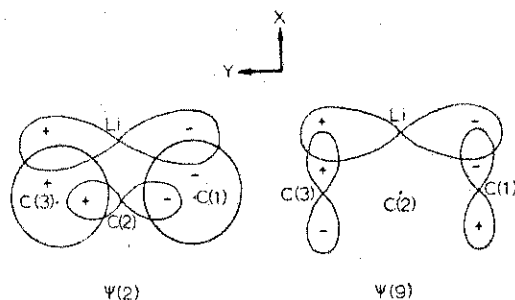
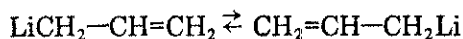


Fig. 3. Molecular orbital sketches of  $\psi(2)$  and  $\psi(9)$ .

remained unchanged, (2) in the allyllithium MO's, with few exceptions, (1,2,3,6, and 9) (see Table 1), the carbon atom coefficients exhibited small decreases as compared to their coefficients in the allyl anion, and (3) all the occupied MO's except the lowest occupied MO were further stabilized in allyllithium. From the electron densities, the partial charges are  $-0.36$  and  $+0.10$  on C(1) and C(2) in the allyl anion and  $-0.20$  and  $+0.16$  in allyllithium. The partial charge on lithium is  $+0.12$  with the rest of the positive charge dispersed among the hydrogens.

#### *Ionic character*

Due to experimental difficulties, limited experimental values are available with which to compare the results of theoretical calculations for allyllithium. The proton magnetic resonance (PMR) spectra is available and is of particular interest as to equivalence of the hydrogen atoms of allyllithium [9]. The room temperature PMR spectra of allyllithium has an  $AB_4$  type spectrum and upon lowering the temperature to  $-87^\circ$  an  $AA'BB'C$  type spectrum was obtained. The following rapid dynamic equilibrium is suggested to account for the PMR data, that being the intramolecular exchange of the lithium from one terminal carbon to the other [10]. The results of the calculations of the propylene-type



arrangement with the Li-C(1) bond distance of  $2.10 \text{ \AA}$  predicts that the LEC described earlier is more stable by  $3.9 \text{ eV}$ . CNDO/2 calculations under the original parameterization are known to give excessive binding energies, therefore, the energies in this paper are used only in describing relative stabilities [4]. The  $AB_4$  type spectra would be the result of rapid intramolecular exchange in this configuration with rotation about the carbon-carbon single bond and the low temperature spectra would correspond to the geometry of the LEC.

Another configuration considered is that of the lithium atom being involved in an intermolecular exchange between allyl fragments. To account for the PMR data, rotation about the carbon-carbon bonds in allyllithium and allyl anion were also calculated and the rotational barriers are predicted to be  $2.5$  and  $1.9 \text{ eV}$ , respectively, the difference between these two configurations being the result of the nuclear-nuclear repulsion for the lithium atom and the allyl fragment. Therefore, assuming the same solvation effects for all three mechanisms, the lowest energy path favors the formation of the allyl anion.

This proposed ionic character is supported by other data. The infrared spectra has a lower than expected carbon-carbon stretching frequency compared to other allyl-metal (Mg, Zn, Cd) compounds [11]. The interpretation of the low temperature PMR spectra by West, Purmont and McKinley concluded that this is not indicative of a covalently bonded allyllithium involved in rapid intramolecular exchange [9]. The calculated dipole moment (a property which CNDO/ calculations are noted for predicting with good success) for allyllithium is 3.6 debyes, which is indicative of charge separation supporting ionic character.

#### Vibrational motions

Several vibrational motions of the lithium in allyllithium for the LEC were considered. Three displacements corresponding to the motions considered are given in Fig. 4. A plot of the total energy versus the lithium displacement (increments of 0.02 Å) about the equilibrium geometry predicts that the motion of the lithium perpendicular to the plane of the allyl fragment (a) is the lowest in energy. This motion maintains the greatest degree of bonding even as the lithium atom coordinates are being varied due to the bonding combination of the lithium  $p_y$ -orbital with the anti-symmetric combination of the terminal carbon  $p$ -orbitals in the highest occupied molecular orbital. Similar vibrational motions have been proposed for lithium naphthalide to account for calculated spin densities obtained from experimental ESR coupling constants [6].

#### Dimer configurations

Solvent studies indicate dimer formation as well as higher degrees of aggregation depending on the concentration [9]; therefore, it was of interest to determine the predicted geometry of the dimer. Utilizing the LEC of the monomer of allyllithium, various dimer geometries were investigated. One possible dimer arrangement, where a lithium atom from one monomer would be bonded to another lithium of the second monomer, was found to have a negative charge localized on both lithium atoms. This, together with the fact

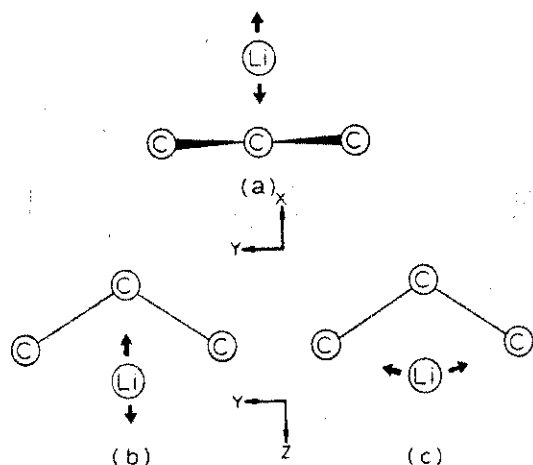


Fig. 4. Vibration motions of the lithium atom: (a) motion of lowest energy; perpendicular to the allylic plane; (b) motion which increases the overlap with the terminal carbons but increases the interaction of the positive charged lithium and center carbon; (c) oscillatory motion which could lead to a propylene-type conformation.

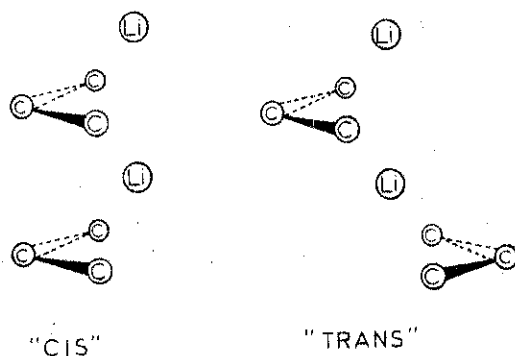


Fig. 5. The conformation of the "cis" and "trans" dimers.

that no lithium containing molecules have shown evidence of direct lithium—lithium bonding, except the lithium molecule, eliminated this geometry from further consideration. In terms of the energies only two possible forms were found significant and are given in Fig. 5. The "cis" dimer was predicted to be 4.6 eV more stable than the "trans" dimer. The total binding energy was predicted to be 8.4 eV more stable for the "cis" dimer compared to the monomer [i.e.  $E(\text{dimer}) - 2E(\text{monomer})$ ]. For the "cis" and "trans" dimers, the more stable molecular orbitals are localized on individual allyl monomeric units and the less stable are spread over the entire dimer. This delocalization provides the additional stability of the dimer as compared to the monomers. Studies of allyllithium in higher concentrations in THF have aggregation greater than ten; the "cis" dimer can easily be extended by "stacking" additional monomeric units in agreement with this observation.

#### Solvent interactions

Experimental studies of allyllithium requires a donor solvent such as ethyl ether or tertiary amine to stabilize the reactive species. These solvents are thought to stabilize allyllithium by formation of intimate ion pairs thereby reducing the magnitude of charge on the lithium atom. Calculations of the interactions of solvent molecules with allyllithium are of interest to determine what changes are predicted by comparing the results of the solvated and unsolvated species. These calculations for ethyl ether or tertiary amine exceeds the computational space available; therefore, the solvent effects are investigated by assuming the solvent to be ammonia as the interactions are expected to be similar to the other solvents. This section contains a discussion of the results obtained for allyllithium solvated with two molecules of ammonia. It was necessary to determine the predicted geometry for the complex before the results of the different forms could be compared. The number of possible displacements that could be considered even for this small complex is great, therefore restrictions were placed on the number of parameters considered. The parameters considered for the predicted geometry were (1) the N—Li—N bond angle, (2) the N—Li bond distance, and (3) the separation of the solvated lithium from the allyl plane.

Crystal structure data for several compounds containing lithium in an analogous environment to that of the complex has been reported by Stucky and co-workers [7, 12]. This data for fluorenyllithium diquinuclidine was used as the starting point for the determination of the predicted geometry. Certain approximations were made with respect to the solvent-lithium interactions. The allyl fragment was assumed to be unchanged from the unsolvated form. Each ammonia molecule was assumed to be equally separated from the lithium atom with H-N-H bond angles of  $107.3^\circ$  and N-H bond distances of  $1.008 \text{ \AA}$ . The results of the calculations predicts that the N-Li-N bond angle of  $109^\circ$  is more stable than the  $123^\circ$  of fluorenyllithium diquinuclidine due to the size of the groups containing the nitrogen atoms. Using the  $sp^3$  tetrahedral bond angle for the N-Li-N component the N-Li distance was varied to determine the minimum energy. The N-Li bond distance is predicted to be  $2.20 \text{ \AA}$  which is slightly longer than the average value of  $2.03 \text{ \AA}$  for the fluorenyllithium diquinuclidine [12] but very comparable to that bond distance for other complexes.

Since it has been observed experimentally that the solvated form of lithium is more stable than the unsolvated form and the results of the calculations agree with this observation, it is of interest to determine what is predicted for the separation of the solvated lithium atom and the allyl fragment. The results of the calculations predict that this separation is increased by  $+0.10 \text{ \AA}$  when the lithium atom of the molecule is solvated by ammonia compared to the unsolvated compound. The changes in electron densities for this lowest energy geometry is given in Fig. 6. The expected effect of the solvent was to decrease the positive charge at the lithium atom. In the unsolvated form a positive charge of  $+0.12$  is predicted while in the solvated form the charge is  $-0.23$  due to the sharing of electron density of the nitrogen atoms. It is of additional interest to determine the changes in bonding between the allyl group in the two forms. Mulliken overlap population values would be expected to be indicative of these changes and the resulting values are given in Table 2. The results indicate that the

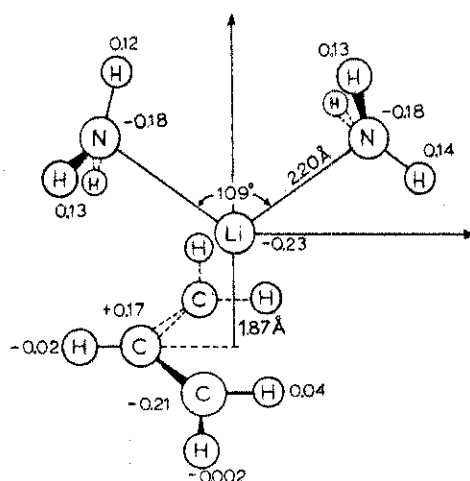


Fig. 6. The predicted geometry for allyllithium solvated with two molecules of ammonia. The nitrogen-lithium and allyllithium fragment separations were varied to determine the energy minimum. The numerical values are the predicted electron densities from the calculations.



TABLE 2

OVERLAP POPULATION VALUES FOR SPECIFIC LITHIUM BONDS

Bonds	Unsolvated	Solvated	Differences
Li-C <sub>1</sub>	0.37	0.34	0.03
Li-C <sub>2</sub>	0.34	0.29	0.05
Li-N <sub>1</sub>		0.28	
Li-N <sub>2</sub>		0.25	

largest change is for the lithium and the central carbon of the allyl fragment. The difference for the two nitrogen atoms are due to the asymmetry with respect to the allyl fragment (see Fig. 6 for labels).

### Conclusions

The results of CNDO/2 molecular orbital calculations predict that the lowest total energy geometry of allyllithium is a nonplanar "bridged" structure. Although the degree of hybridization on the lithium has not been computed, the resulting molecular orbitals reflect that the  $p_y$  orbital (in our coordinate system) on lithium is principally involved in the bonding with admixtures of the remaining valence orbitals between lithium and the carbon atoms in this molecule. A large calculated dipole moment and large localized charges on the atoms suggest that allyllithium is appreciably ionic and will interact strongly with donating solvents. The predicted geometry for the dimer, using the results for the monomer, is a "stacked" structure which is capable of being extended to higher degrees of aggregation.

The interactions of ammonia as the donor solvent with allyllithium have been considered. The solvated species is predicted to be more stable than the neat compound in agreement with experimental observations. The geometry of the solvated species is predicted to be slightly altered, compared to the unsolvated species the separation of the allyllithium fragment increased by +0.10 Å. The calculated electron density changes are as expected with the donor solvent decreasing the positive charge on the lithium atom. Mulliken overlap populations predict a decrease in the bonding between the lithium and allyl fragment with the greatest change for the central carbon of the allyl fragment.

It would be most informative to make X-ray crystallographic studies on allyllithium, or donor solvent complexes thereof, to determine its structure and possible bonding mechanisms. <sup>13</sup>C NMR chemical shift data would also aid in the establishment of allyllithium's ionic character.

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