CHAPTER - V

π-ELECTRONIC POLARIZABILITY OF BUTADIENE*

* "π-Electronic Polarizability of Cis and Trans-Butadiene"
  T. Radhakrishna and Vijay Kumar,
  and
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5.1: Introduction

The SCF-MO theory used to obtain the wave functions used in the earlier chapter involves not only the \( \pi \)-electron approximation but also the evaluation of certain integrals in a semi-empirical way. While this approach gives a fairly satisfactory account of the \( \pi \)-electronic structure of conjugated molecules, it is nevertheless a semi-empirical approach making use of experimental quantities. In order to test the present hypothesis, regarding the relationship between the electronic polarizability and the electronic transitions, using ab initio wave functions, calculations have been made for cis- and trans-butadiene using such wave functions.

5.2: Details of the MO calculations

Parr and Mulliken\(^1\) have carried out a LCAO-MO-SCF calculation of butadiene using Roothaan's method\(^2\) and treating butadiene as a four electron problem, that is, within the framework of the \( \pi \)-electron approximation. In this method all the integrals involved have been calculated explicitly and no semi-empirical quantity has been used. Use has been made of the symmetry of the molecules for simplifying the calculations. The molecular orbitals and the transition energies obtained by them are given in Tables 5.1 and 5.2 for cis- and trans-butadiene, respectively.
### TABLE - 5.1

**CIS-BUTADIENE**

**Geometry**

\[ R_{c_2c_3} = 1.46 \text{ \AA}^0 \]

\[ R_{c_1c_2} = R_{c_3c_4} = 1.35 \text{ \AA}^0 \]

<table>
<thead>
<tr>
<th>Molecular Orbitals</th>
<th>( \varphi_1 )</th>
<th>( \varphi_2 )</th>
<th>( \varphi_3 )</th>
<th>( \varphi_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varphi_1 )</td>
<td>0.3484</td>
<td>0.4719</td>
<td>0.4719</td>
<td>0.3484</td>
</tr>
<tr>
<td>( \varphi_2 )</td>
<td>0.5106</td>
<td>0.4222</td>
<td>-0.4222</td>
<td>-0.5106</td>
</tr>
<tr>
<td>( \varphi_3 )</td>
<td>0.6439</td>
<td>-0.4662</td>
<td>-0.4662</td>
<td>0.6439</td>
</tr>
<tr>
<td>( \varphi_4 )</td>
<td>0.5373</td>
<td>-0.7276</td>
<td>0.7276</td>
<td>-0.5373</td>
</tr>
</tbody>
</table>

Computed excitation energies (in ev) of excited states using the above molecular orbitals

<table>
<thead>
<tr>
<th>Energy</th>
<th>( \varphi_2 + \varphi_3 )</th>
<th>( \varphi_1 + \varphi_3 )</th>
<th>( \varphi_2 + \varphi_4 )</th>
<th>( \varphi_1 + \varphi_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon_j - \epsilon_1 )</td>
<td>12.470</td>
<td>15.254</td>
<td>16.069</td>
<td>18.853</td>
</tr>
<tr>
<td>( J_{ij} )</td>
<td>9.461</td>
<td>9.291</td>
<td>9.524</td>
<td>10.021</td>
</tr>
<tr>
<td>( K_{ij} )</td>
<td>2.395</td>
<td>2.178</td>
<td>2.282</td>
<td>1.759</td>
</tr>
<tr>
<td>( E_{vij} - E_N )</td>
<td>7.799</td>
<td>10.319</td>
<td>11.129</td>
<td>12.350</td>
</tr>
</tbody>
</table>
### Table 5.2

**Trans-Butadiene**

#### Molecular Orbitals

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
<th>$\gamma_3$</th>
<th>$\gamma_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_1$</td>
<td>0.3540</td>
<td>0.4687</td>
<td>0.4687</td>
<td>0.3540</td>
</tr>
<tr>
<td>$\phi_2$</td>
<td>0.5081</td>
<td>0.4229</td>
<td>-0.4229</td>
<td>-0.5081</td>
</tr>
<tr>
<td>$\phi_3$</td>
<td>0.6452</td>
<td>-0.4698</td>
<td>-0.4698</td>
<td>0.6452</td>
</tr>
<tr>
<td>$\phi_4$</td>
<td>0.5343</td>
<td>-0.7268</td>
<td>0.7268</td>
<td>-0.5343</td>
</tr>
</tbody>
</table>

Computed excitation energies (in ev) of excited states using the above molecular orbitals

#### Excitation

<table>
<thead>
<tr>
<th>Energy</th>
<th>$\phi_2 \rightarrow \phi_3$</th>
<th>$\phi_1 \rightarrow \phi_3$</th>
<th>$\phi_2 \rightarrow \phi_4$</th>
<th>$\phi_1 \rightarrow \phi_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi_j - \xi_1$</td>
<td>12.451</td>
<td>15.291</td>
<td>16.040</td>
<td>18.880</td>
</tr>
<tr>
<td>$J_{1j}$</td>
<td>9.315</td>
<td>9.218</td>
<td>9.429</td>
<td>9.956</td>
</tr>
<tr>
<td>$K_{1j}$</td>
<td>2.551</td>
<td>2.087</td>
<td>2.169</td>
<td>1.828</td>
</tr>
<tr>
<td>$E_{v1j} - E_N$</td>
<td>8.238</td>
<td>10.247</td>
<td>10.949</td>
<td>12.580</td>
</tr>
</tbody>
</table>
In the present work the transition moment matrix elements were evaluated using these wave functions and the planar geometry for the carbon skeleton of cis- and trans-butadiene based on the electron diffraction results of Schomaker and Pauling.3

The experimental value of the \( \pi \)-electronic polarizability \( (\alpha_{\pi}) \) is obtained by subtracting the bond refractions of the \( \pi \)-skeleton \( (R_\pi) \) from the experimental molar refraction \( (R) \) and using the relation:

\[
R_\pi = R - R_\pi = \frac{4}{3} \pi N \alpha_{\pi}
\]

where \( N \) is the Avagadro number. Bond refraction values of Denbigh4 were used for the bonds in the \( \pi \)-skeleton. The value of the \( \pi \)-electronic polarizability \( (\alpha_{\pi}) \) thus obtained for butadiene is \( 28.9 \times 10^{-25} \text{ cm}^3 \). While it is not clear whether the experimental value of molar refraction pertains to cis- or trans-butadiene, it is significant that according to the electron diffraction study of butadiene in the vapour state, it exists almost exclusively in the trans-form.5 Under these circumstances the experimental value of \( \pi \)-electronic polarizability \( (\alpha_{\pi}) \) obtained above may be taken to be that of trans-butadiene.

5.3: Results and Discussion

The theoretical values of \( \pi \)-electronic polarizability evaluated on the above basis and the contribution of the
various transitions to it are presented in Table 5.3. It can be seen that the agreement between the theoretical and experimental values is quite good.

<table>
<thead>
<tr>
<th>Orbital transition</th>
<th>Theoretical $\pi$-electronic polarizability $\times 10^{25}$ cm$^3$</th>
<th>Experimental $\pi$-electronic polarizability $\times 10^{25}$ cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis-butadiene</td>
<td>trans-butadiene</td>
</tr>
<tr>
<td>$\Phi_2 \rightarrow \Phi_3^*$</td>
<td>12.5</td>
<td>25.00</td>
</tr>
<tr>
<td>$\Phi_2 \rightarrow \Phi_4^*$</td>
<td>8.3</td>
<td>0</td>
</tr>
<tr>
<td>$\Phi_1 \rightarrow \Phi_3^*$</td>
<td>4.3</td>
<td>0</td>
</tr>
<tr>
<td>$\Phi_1 \rightarrow \Phi_4^*$</td>
<td>0.2</td>
<td>3.2</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td><strong>25.3</strong></td>
<td><strong>28.2</strong></td>
</tr>
</tbody>
</table>

There are two extreme configurations of planar butadiene, cis and trans, which are distinguished by the geometry around the $C_2 - C_3$ bond, belonging to the point groups $C_{2v}$ and $C_{2h}$.

The ground state configuration of butadiene, ignoring the $\sigma$-electrons is $\Phi_1^2 \Phi_2^2$. There are four excited configurations arising from one electron promotions. Excitation to these states gives rise to four absorption bands. The symmetry species of the excited states, the effect of selection rule on the transitions$^6$ and the percentage contribution of these transitions to the $\pi$-electronic polarizability evaluated on the basis of the present work are presented in Table 5.4.
For trans-butadiene, the first $^{1}B_u \leftrightarrow ^{1}A_g$ transition contributes 89 per cent to the $\pi$-electronic polarizability while the second transition contributes 11 per cent. The two $^{1}A_g \leftrightarrow ^{1}A_g$ do not make any contribution as the transition moment matrix elements turns out to be zero. This result is in accordance with the prediction of the symmetry selection rules according to which these transitions are forbidden.

In the case of cis-butadiene, however, the first $^{1}B_2 \leftrightarrow ^{1}A_1$ transition makes only a 50 per cent contribution to the $\pi$-electronic polarizability, and the second $^{1}B_2 \leftrightarrow ^{1}A_1$ transition only 1 per cent. On the other hand the first $^{1}A_1 \leftrightarrow ^{1}A_1$ transition contributes as much as 32 per cent while the second $^{1}A_1 \leftrightarrow ^{1}A_1$ transition makes 17 per cent. So that between them the two $^{1}A_1 \leftrightarrow ^{1}A_1$ transitions account for almost half of the $\pi$-electronic polarizability. This result is significant in view of the fact that these transitions are expected to be weak$^6$ and are liable to be under-emphasized or even ignored in the context of polarizability considerations.

5.4: Polarizability of Isomers

Theoretical calculations$^1$ as well as the experimental evidence$^7,^8$ indicates that trans-butadiene is more stable than the cis-form. It is interesting to note that the energetically more stable isomer, trans-butadiene, has higher
polarizability compared to cis-butadiene. The possible relationship between stability and polarizability, for geometrical isomers, needs to be further explored.
REFERENCES


2  Roothaan, C.C.J., Rev.Mod.Phys., 23, 69 (1951)


7  Mulliken, R.S., Rev.Mod.Phys., 14, 265 (1942)