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Pi-electronic polarizability of cis and trans-butadiene

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1. INTRODUCTION

Molecules with conjugated double bonds do not conform to the additivity scheme of atomic and bond refractions, giving rise to the concept of optical exaltation or exaltation of refraction[1]. The anamolously high refraction of such molecules has been ascribed to the delocalized, mobile pi-electrons, which require smaller excitation energies.[2,3,4] Consideration of the spectroscopic aspects of molar refractions has shown that the refraction of the separate portions of the molecule results from various absorption bands.[5,6] According to the principle of the seperability of sigma and pi-electrons, the molar refraction of a conjugated system can be divided into the refraction of the core, which should remain in the additivity scheme and the refraction of the pi-electrons, which consist of increments of double bonds and optical exaltation. Correspondingly we have the sigma and pi components of electronic polarizability[7]. In the present work the relationship between the pi-electronic absorption and pi-electronic polarizability has been investigated quantitatively for cis and trans-butadiene using molecular orbital wavefunctions.

2. DETAILS OF CALCULATIONS

The polarizability in the direction of principal axis of the polarizability tensor is given by[8] :

$$\alpha_{xx}(\nu_0) = \Sigma_k \frac{2|\mu_x|^2_{lk}\ (E_k - E_l\ )}{(E_l\ - E_k)^2 - (h\nu_0)^2} \tag{1}$$

and the polarizability avaraged over all directions is :

$$\alpha\ (\nu_0) = {}^1/_3\ [\alpha_{xx}\ (\nu_0) + \alpha_{yy}\ (\nu_0) + \alpha_{zz}\ (\nu_0)] \tag{2}$$

where $(\mu_x)_{lk}$ is the transition moment matrix for the transition between the energy states characterised by energies E_l and E_k and ν_0 is the frequency of the incident electromagnetic radiation. The pi-electronic polarizability can be calculated from (1) if the appropriate wavefunctions are known.

In the present work LCAO-SCF wavefunctons and energies[9], for cis and trans-butadiene, obtained with 2Pπ—Slater atomic orbitals on the four carbon atoms and Roothaan's method[10]. were used. This gives four best ground state molecular orbitals, φ_1, φ_2 (filled) and φ_3^*, φ_4^* (vacant). The excitation of an electron from the molecular orbitals φ_i to φ_j gives rise to an excited state. The energy of the singlet excited state with respect to the ground state is given by :

$$E \quad - E_N = (\varepsilon_i - \varepsilon_i) - J_j$$

where the ε^s are the orbital energies and J_{ij} are the coulomb repulsion integrals over the molecular orbitals.

The orbital transition moment matrix is given by

$$M_{ij} = <\varphi_i \, |\gamma| \varphi_j > \qquad (3)$$

for a transition from molecular orbitals
This can be expressed in terms of atomic orbitals as

$$M_{ij} = \sum_{p,q} C_{pi} \; C_{qj} <\chi_p |\gamma| \chi_q > \qquad (5)$$

Where the C's are the coefficients of the atomic orbitals χ_p and χ_q centered on atoms p and q, in the molecular orbitals. The transition moment matrix element over the atomic orbitals were evaluated using the relation[11].

$$<\chi_p |\bar{r}| \chi_q > = {}^1/_2 \, S_{pq} \; (\bar{r}_p + \bar{r}_q) \qquad (6)$$

Where S_{pq} is the overlap integral and $\bar{r}_p$ and $\bar{r}_p$ are the vectors from the origin to p and q respectively.

The planar geometry assumed for the carbon skeletons of cis and trans-butadiene, is based on the electron diffraction results of Schomaker and Pauling[12].

The experimental value of the Pi-electron polarizability ($\alpha_{e\pi}$) is obtained by subtracting the bond refractions of the sigma skeleton (R_σ) from the experimental molar refraction (R) and using the relation :

$$R_\pi = R - R_\sigma = {}^4/_3 \, \pi N \alpha_{e\pi}$$

Where N in the Avogadro number. Bond refraction values of Denbigh[18] were used for the bonds in the sigma skeleton. The value of the pi-electronic polarizability $(\alpha_{e\pi})$ thus obtained for butadiene is 28.9×10^{-25}. 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[14]. Under these circumstances the experimental value of pi-electronic polarizability $(\alpha_{e\pi})$ obtained above may be taken to be that of trans-butadiene.

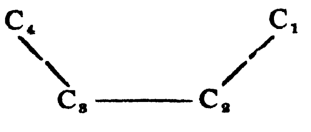
The theoretical values of pi-electronic polarizability evaluated on the above basis and the contribution of the various transitions to it are presented in table 1. It can be seen that the agreement between the theoretical and experimental values is quite good.

Table 1.

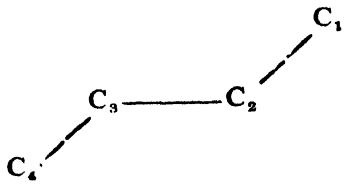
Orbital Transition.	Theoretical Pi-electronic Polarizability $\times 10^{25}$		Experimental Pi-electronic Polarizability $\times 10^{25}$
	Cis Butadiene	Trans Butadiene	
$\varphi_2 \rightarrow \varphi_3^*$	12.5	25.0	—
$\varphi_2 \rightarrow \varphi_4$	8.3	0	—
$\varphi_1 \rightarrow \varphi_3^*$	4.3	0	—
$\varphi_1 \rightarrow \varphi_4^*$		3.2	—
Total	25.3	28.2	28.9

3. DISCUSSION

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}



Cis-butadiene
C_{2v}



trans-butadiene
C_{2h}

The ground state configuration of butadiene, ignoring the sigma electrons is $\varphi_1^2\ \varphi_2^2$. There are four excited configurations arising from one electron promotions. Excitation to these states gives rise to four absorption bands. The symmetry spieces of the excited states the effect of selection rule on the transitions[15] and the percentage contribution of these transitions to the pi-electronic plarizability evaluated on the basis of the present work are presented in table 2.

For trans-butadiene, the first ${}^1B_u \leftarrow {}^1A_g$ transition contributes 89% to the pi-electronic polarizability while the second transition contributes 11%. This is in conformity with the generally held view that in conjugated molecules the longest wavelength contribution determines the pi-electronic polarizability. The two ${}^1A_g \leftarrow {}^1A_g$ 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 ${}^1B_2 \leftarrow {}^1A_1$ transition makes only a 50% contribution to the pi-electronic polarizability, and the second ${}^1B_2 \leftarrow {}^1A_1$ transition only 1%. On the other hand the first ${}^1A_1 \leftarrow {}^1A_1$ transition contributes as much as 32% while the second ${}^1A_1 \leftarrow {}^1A_1$ transition makes 17%. So that between them the two ${}^1A_1 \leftarrow {}^1A_1$ transitions account for almost half of the pi-electronic polariziability. This result is significant in view of the fact that these transitions are expected to be weak[15] and are liable to be underemphasised or even ignored in the context of polarizability considerations.

Thoretical calculations[9] as well as the experimental evidence[16,17] 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.

4. CONCLUSION

The relationship between optical absorption and electronic polarizability has been quantitatively investigated. The pi-electronic polarizability for butadiene has been calculated in good agreement with experimental value and the contribution of various transitions to the electronic polarizability has been evaluated. The present results seem to encourage the use of the dispersion formula for polarizability calculations for molecules, provided good quality

Table 2.

Configuration	Transitions	Cis-Butadiene			Trans-Butadiene		
Ψ_i $(\varphi_1^2\varphi_2^2)$		(C_{2v})			(C_{2h})		
		A_1			A_g		
		Symmetry	Selection Rule	% Contribution to	Symmetry	Selection Rule	% Contribution to
Ψ_{f1} $(\varphi_1^2\varphi_2\varphi_3^*)$	$\Psi_i \rightarrow \Psi_{f1}$	B_2	Allowed	50	B_u	Allowed	89
Ψ_{f2} $(\varphi_1^2\varphi_2\varphi_4^*)$	$\Psi_i \rightarrow \Psi_{f2}$	A_1	Allowed	32	A_g	Forbidden	0
Ψ_{f3} $(\varphi_1\varphi_2^2\varphi_3^*)$	$\Psi_i \rightarrow \Psi_{f3}$	A_1	Allowed	17	A_g	Forbidden	0
Ψ_{f4} $(\varphi_1\varphi_2^2\varphi_4^*)$	$\Psi_i \rightarrow \Psi_{f4}$	B_2	Allowed	1	B_u	Allowed	11

wavefunctions are used. It must however be remembered that transitions to the continuous, as well as to the discrete energy states must be included in the summations and that the effect of continua is difficult to estimate[18].

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