ULTRAVIOLET LINEAR DICHROISM STUDIES OF INDENE

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Abstract

Ultraviolet Linear Dichroism (LD) spectra of the indene molecule in stretched polyethylene (PE) film are reported. Differently polarized electronic transitions are resolved in the LD spectrum. The first electronic transition at λ_{max} = 285 nm, which is hidden by the second one in solution, is clearly isolated in LD spectra and polarized along the long axis of the molecule. The second one which is located at about λ_{max} = 250 nm is polarized along the short axis. The calculated spectrum of indene shows the same trends in complete agreement with experimental findings.

1. Introduction

Indene (Fig 1) has been the subject of numerous theoretical and experimental papers [1-14] because of its chemical and biological importance. This compound is a prototype of systems in which π-electrons in the ethylenic bond and the phenyl ring have strong interactions. Moreover, the evolution of the hyperconjugative ratio of CH_2 group determines the main physicochemical properties of indene [15]. The study of the electronic spectrum and spectroscopic properties of this molecule provides valuable information on its photochemical reactivity. With the aim to characterize correctly the first electronic transitions, we have studied the absorption spectrum of indene with respect to the polarization directions of UV transitions using linear dichroism in an anisotropic host of stretched polyethylene. Such measurements give information about the number, position and polarization of the electronic transitions [16-17]. On the other side , the CNDO/M semiempirical calculations [18] are applied to elucidate the assignments of the UV absorption spectrum.

2. Materials and methods

2.1 Chemicals

Indene was purchased from FLUKA and used without further purification. It was introduced into polyethylene (PE) sheet from solution in butyl-chloride (FLUKA; spectral quality). The film was stretched four times from its starting length.
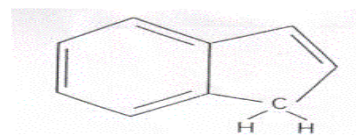
Figure 1: Structure of indene.

2.2 Polarized UV measurements

The spectra were performed on a CARY 118 spectrophotometer equipped with two rotatable Glan prism polarizers in the sample and reference beams.

2.3 Linear Dichroism (LD)

LD is defined as : $LD = A_{//} - A_{\perp}$
Where $A_{//}$ and $A_{\perp}$ are the absorbances measured with plane polarized light parallel (//) and perpendicular ($\perp$) to the unique sample axis
(the stretching direction of the film).
The reduced linear dichroism is defined as :
$LD^r = LD/A_{iso}$
where A_{iso} is the absorbance of a corresponding isotropic sample.
For an uniaxial sample such as the stretched polyethylene film, the isotropic absorbance can be calculated from the polarized components as [19] :
$A_{iso} = 1/3 (A_{//} + 2A_{\perp})$
the orientation K_i factor [20-23] which describes the middle alignment of the transition moment M_i is defined as : $K_i = <\cos^2(M_i ; u)>$
Where $(M_i ; u)$ is the angle between the transition moment M_i and the streching direction u, the

angle brackets indicate averaging over all molecules under observation.

The determination of the orientation K_i factor is dependent on the nature of the spectra. In the UV absorption spectra where the bands are broad and overlap, the trial and error method (TEM) [20 –23] is used in order to reduce the uncertainty of the K_i value. This method is based on the stepwise formation of linear combinations of polarized spectra; $r_k(\lambda)$ [21, 24, 25] is written as :

$$r_k(\lambda) = (1-K) A_{//}(\lambda) - 2 KA_{\perp}(\lambda)$$

The transition moment having the highest K value is the best aligned with the long molecular axis (L) which is normal to the smallest cross section of the molecule and the best aligned one with the stretching direction u [20]. The axis, which is the worst aligned with the stretching direction , coincides with one of the short axes of the molecule (i.e the in-plane axis or the axis perpendicular to the plane of chromophore). Furthermore, the transition moment with the lowest K value is, on the average, the worst aligned with the stretching direction.

2.4 CNDO/ M Calculations

Theoretical semiempirical calculations using the CNDO/M method have been performed to characterize the UV transitions on indene at the molecular geometry reported in the literature [26]. Sixty singly excited configurations were determined making use of the configuration interaction treatment implemented in the CNDO/M procedure to explore excited states.

3. Results and discussion

In the UV observed spectra of indene in two solvents with different polarity, hexane and ethanol (Fig 2), a strong band located about 250 nm and a weak absorption between 280 and 290 nm have been observed in both solvents.
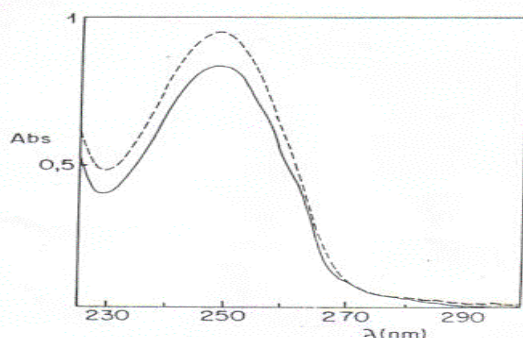
Figure 2 : Absorption spectra of indene in hexane (…) and ethanol (—) at room temperature, (C=10^{-4})

The absorbance curves $A_{//}(\lambda)$ and $A_{\perp}(\lambda)$ (Fig3) are resolved better than those obtained in solutions. Furthermore, the LD^r spectrum which permits the determination of the number of electronic transitions in the absorption spectrum [17-27], is resolved into two components in the spectral range of 230-300 nm.
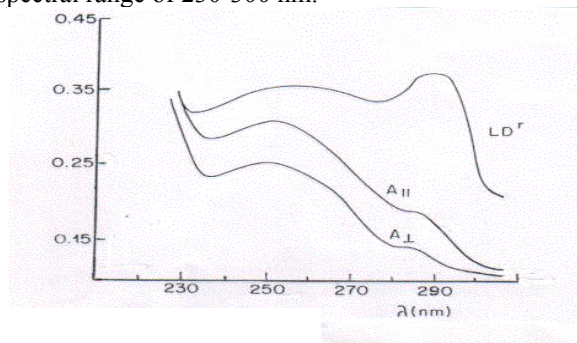
Figure 3 : Absorbance curves $A_{//}$; $A_{\perp}$ and LD^r spectrum for indene aligned in stretched PE film at room temperature .

However, in this interval the LD^r curve shows two main values : 0.425 and 0.362. Accordingly, the strong band observed in the UV spectra is the envelope of two pure π-π^* electronic transitions with distinct polarization [27].

The transition moment directions relative to the molecular orientation axis are determined by the linear combination $r_k(\lambda)$ [20-22], where the K value is systematically varied from 0 to 1 in steps of 0.1 [24, 25] (Fig 4).
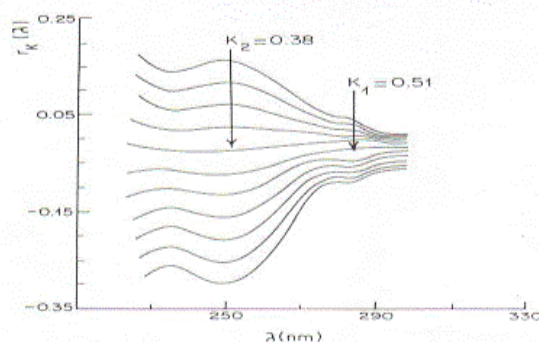
Figure 4 : Stepwise spectral reduction. $r_k(\lambda) = (1-K) A_{//}(\lambda) - 2K A_{\perp}(\lambda)$ for indene. K is varied between 0 and 1 in steps of 0.1.

These series of linear combinations are constructed in such a way that the contribution of the jth transition at the moment M_j vanishes when

K= K_j in the $r_k(\lambda)$ linear combination. The L_b and L_a electronic transitions which are located about 285 and 250 nm , have orientation factors K_1 = 0.51 and K_2 = 0.38, respectively. It can be concluded that the polarization directions of the transitions close to 285 and 250 nm form tow different angles with the orientation axis, one relatively small and the other relatively large. These LD measurements do not allow to obtain any precise experimental values of the angles θ_i between the transition moments M_i and the long axis of indene. Therefore, the observed K_i values only provide qualitative information on the alignment of the transition moments M_i with respect to the long axis. We report in figure 5 the most probable zone where the polarization direction of the two electronic transitions of indene might be situated.

The CNDO/M method predicts two π-π^* electronic transitions in the low energy region for indene with the L_b and L_a transitions encountered at 280.35 and 252.47 nm, respectively, so that the observed transitions may be assigned to the calculated ones unambiguously. The theoretical values of the oscillator strengths seem to agree with the relative magnitudes of experimental data. Furthermore, the calculation predicts that the energy of the transition L_b ($S_0 \rightarrow S_1$) is low and its transition moment directed along the long axis, while the second transition L_a ($S_0 \rightarrow S_2$) has the transition moment directed along the short axis. The calculated angle θ_i between the transition moment M_i and the long axis of the molecule is consistent with the observed orientation factor K_i. However, without additional information precise values for the transition moment angles θ_i cannot be determined from the observed orientation factors [24, 25].
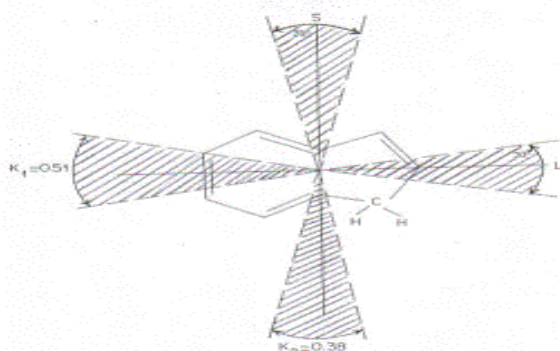
Figure 5: The most probable transition moment directions concluded from the present dichroic study with an inaccuracy of 10°. The lines (L) and (S) are respectively, the approximated long and in-plan short axis of indene.

The simulation of the experimental results was carried out by means of CNDO/M semiempirical calculations. In table 1 the theoretical results are summarized and listed along with the experimental data.

Experimental data			CNDO/M			
λ (nm)	Log ε	K_i	λ (nm)	f	θ_i	Nature
285	0.038	0.51	280.35	0.0082	3°09	π-π^*
250	0.831	0.38	252.47	0.4363	98°57	π-π^*
210	0.438	0.42	210.81	0.2000	75°28	π-π^*

Table 1 : The observed and calculated spectroscopic parameters of singlet-singlet π-π^* transitions of indene.
K_i : Calculated orientation factor from Linear Dichroism Measurements.
f : Oscillator strength.
θ_i : Angle between the transition moment M_i and the long axis of indene.

4. Conclusion

The strong absorption band of indene chromophore is confirmed, by the analysis of the linear dichroism spectra with the help of CNDO/M semiempirical calculations, to be a superposition of two π-π^* electronic transitions with different polarization. However, the electronic transitions at 285 and 250 nm are polarized along the 'long' and 'short in-plane' axes of indene, respectively.

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