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Electronic Structure of Some Chalcone Derivatives . II. Electronic absorption spectra . INDO / S-CI.

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التركيب الإلكتروني لبعض مشتقات الشالكون
II. طيف الامتصاص . INDO / S-CI

تمت دراسة طيف الامتصاص لبعض مشتقات الشالكون في المنطقة فوق البنفسجية باستخدام مذيبات قطبية وغير قطبية . وقد استخدمت طريقة INDO / S-CI لحساب الانتقالات النظرية لهذه المركبات . وبتحليل طيف الامتصاص باستخدام نظرية المدارات الجزيئية أمكن معرفة نوع الانتقال الإلكتروني وتأثير المذيبات المختلفة عليه ومعرفة ما إذا كان الانتقال مُوضعاً أو غير مُوضع أو متغير القيمة وقد لوحظ وجود توافق بين القيم النظرية والقيم العملية لهذه الأنتقالات .

Abstract

The electronic absorption spectra of some chalcone derivatives, namely,1,3-diphenyl –2-propen-1-one, 3-(3-tolyl) –1-phenyl–2- propen-1-one , 3–(4- bromo phenyl) –1– (4–methoxy phenyl)–2-propen-1-one, 3-(3–4- –methylene dioxy phenyl)–1– (4-methoxy phenyl)–2–propen-1–one and 3-(3,4—methylene dioxy phenyl)–1–(4- bromo- phenyl)–2-propen–1–one, have been measured in the UV region using polar and non-polar solvents. INDO/ S-CI calculations were performed to predict the theoretical transitions. Analysis of the computed CI states and the MO's involved enabled the assignment of the observed bands. Their origin was assumed to be due to localized , delocalized or charge transfer transition. Solvent effects on band position and intensities have also been investi- gated.

Key words : UV spectra , Chalcones , INDO/S ,CI calculations.

INTRODUCTION

The biological activity of 1,3- diaryl-propenones (chalcones) attracted the attention to study their properties (Sato *et al.* 1997and Mukherjee *et al*. 2001). The ground state geometric parameters and charge density distributions of some chalcones were determined using AM1-MO treatment (Hameed , *forthcoming*).

The electronic spectra of the studied compounds discussed in this work are rarely reported in the literature. Most of the conclusions that relate the spectra to structures are qualitative (Wheeler *et al*.1946, Katzenellenbogen *et al*.1947, Lutz , *et al*.1950, Kuhn *et al*.1950, Szmant *et al*.1952, Black *et al*.1955, Kline, *et al* 1961, Sukhorukov, *et al.* 1970 , Gineitite , *et al*.1989).

The aim of this work is to explore :

1- The type and extent of conjugative interaction between subsystems of some molecules.
2- The effect of the solvent polarity on the observed spectra and hence , predicting the relative stabilities, extent of charge transfer character and assignment of the observed electronic transitions.
3- The effect of substitution, using electron-donating and withdrawing groups at the para-position of the aromatic ring on the electronic spectra of chalcone derivatives.

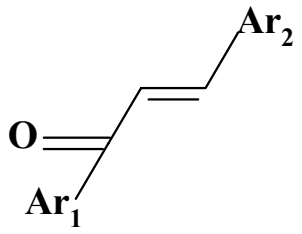
EXPERIMENTAL

The compounds were prepared by the Claisen-Schmidt condensation as descri- bed in the literature.(House, 1972, Claisen *et al.* 1881and Nielsen *et al.* 1986)

The solvents , ethanol and cyclohexane were purified by convenentional method. (Vogel, 3rd.ed. 1965)

The electronic spectra were scanned on a Shimadzu UV260 spectrometer using 1.0 cm path length cells.

Chalcones studied in this work are :



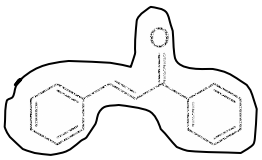
	Ar_2	Ar_1
I.	Phenyl	Phenyl
II.	m- tolyl	Phenyl
III.	P- bromo phenyl	P- methoxy phenyl
IV.	3,4 methylene dioxy phenyl	P- methoxy phenyl
V.	3,4 methylene dioxy phenyl	P- bromo phenyl

Method of calculation :

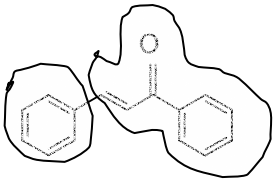
Molecular orbital calculations were performed using the INDO/S method (Oleari *et al.*1985) as implemented in the MOPAC package (QCPE, *version* 7.0 *Department of chemistry , Indiana University*). The energy of the ground state and those of the excited configurations are calculated. Configuration interaction (CI) is then considered between all configurations, involving the highest three occupied and lowest two vacant MO's and the CI-matrix is solved.

RESULTS AND DISCUSSION

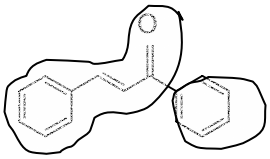
The spectra of 1,3-diphenyl-2-propen-1-one derivatives depended on the type and extent of interaction between the different subsystems. The possible four types of interaction between the different subsystems are shown in the following :



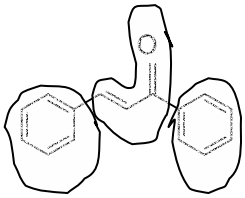
(a)



(b)



(c)



(d)

1- The full conjugation extending over the whole molecule (a), reflects that the system of diphenyl-2-propenone should be completely different from that of its subsystems.

2- Cross conjugation is observed in structures (b), (c) and (d) which reflect an additive spectrum.

The observed wavelengths and the molar extinction coefficients for the studied compounds in ethanol and cyclohexane are presented in Table 1.

a- Electronic absorption spectra of trans-(s-cis)-1,3-diphenyl-2-propen-1- one (I)

Figure 1 presents the electronic absorption spectra of trans-(s-cis)-1,3-diphenyl -2-propen-1-one (I) in cyclohexane and ethanol and shows definite dependence on the solvent polarity. Two absorption regions are recognized , a broad medium intensity

envelope that covers the 280-350 nm region and a short wavelength absorption in the 210-240 nm region. The long wavelength band undergoes a marked red shift of about 12 nm on going from cyclohexane to ethanol i.e. increasing solvent polarity, whereas the second band shows no solvent dependence. Furthermore, solvent polarity has a pronounced effect on the relative intensities of these two absorption bands.

Table 2 presents a comparison of the experimentally observed and theoretically computed spectra in addition to a quantitative assignment of all transitions observed. Figures 2a,2b present the charge density maps of the five MO's considered in the transitions. The long absorption is due to a transition to state with slightly smaller dipole moment and is composed of a major configuration $\theta_{38}^{-1}\ \theta_{41}$ which is a charge transfer from Ar_1 to Ar_2 and acrolein. Thus, the $S_0 \rightarrow S_1$ transition involves a considerable CT and polar solvents will destabilize the ground state to a much greater extent. This explains the observed red shift upon increasing solvent polarity.

The second $(\pi,\pi^*)^1$ state is a mixture of $\theta_{38}^{-1}\theta_{40}$ and $\theta_{37}^{-1}\theta_{40}$. Both are CT from Ar_1 to Ar_2 and acrolein moieties. No solvent dependence can be detected in this transition .The short wavelength $(\pi,\pi^*)^1$ state is predicted at ≈ 205 nm with a very strong intensity in very good agreement with experiment. This state is composed of a mixture of $\theta_{37}^{-1}\ \theta_{40}$ and $\theta_{39}^{-1}\theta_{41}$ configurations. The configuration $\theta_{37}^{-1}\theta_{40}$ which is CT from Ar_1 to Ar_2 and acrolein moieties , whereas the configuration $\theta_{39}^{-1}\theta_{41}$ is a CT from acrolein moiety to Ar_1. This($\pi,\pi^*)^1$ almost possesses the same polarity as the ground state and hence no pronounced solvent effect on band position is expected .

b- Electronic absorption spectra of 1-phenyl-3-(3 ˉ-tolyl)-2-propen-1-one (II)

Figure 3 presents the electronic absorption spectra of (II) in ethanol and cyclo- hexane. The long wavelength band centered at 283 nm (ε = 32230) in cyclohexane and at 298 nm (ε =21485) in ethanol. The second band centered at 235 nm (ε = 12805) in both solvents. The short wavelength in both solvents centered at 205 nm (ε = 30150). The effect of methyl substitution on the observed spectrum is, intensification and slight perturbation of band position ; a typical behavior due to its inductive effect. Table 3 presents a comparison of the experimentally observed and theoretically computed spectra in addition to a quantitative assignment of all transitions observed .

The long wavelength absorption is composed of one main configuration $\theta_{41}^{-1}\theta_{44}$ which is CT from Ar_2 to $Ar_1$and acrolein moieties. Thus $(\pi\ ,\pi^*)^1$ state would experience a red shift upon increasing solvent polarity , in agreement with experiment.

The second $(\pi,\pi^*)^1$ state is composed of a linear combination of three configur- ations, $\theta_{41}^{-1}\theta_{43}$ (CT $Ar_2 \rightarrow Ar_1$ + acrolein),$\theta_{42}^{-1}\ \theta_{44}$ (CT Ar_2 +acrolein $\rightarrow Ar_1$)and $\theta_{40}^{-1}\ \theta_{43}$ (CT $Ar_1 \rightarrow$ acrolein).This band shows no solvent dependence.

The short wavelength absorption centered at 205 nm is composed of one main configuration $\theta_{40}^{-1}\ \theta_{43}$ which is CT from $Ar_1 \rightarrow$ acrolein .

c- Electronic absorption spectra of 3-(4'-bromophenyl)–1-(4' -methoxy-phenyl)–2- propen-1-one (III)

Fig. 4 presents the electronic absorption spectra of (III) in polar and non-polar solvents. Table 4 represents the state transition computed theoretically, assignment, observed and calculated transitions energy.

The spectrum in both solvents is similar to the previous derivatives in shapes but different in intensities. The spectrum in cyclohexane is composed of two main bands. A broad long wavelength band centered at 315 nm (ε =36425). A medium band centered at 225 nm (ε=16723). The spectrum in ethanol composed of three bands centered at 320 nm (ε =34955) , 225 nm(ε =12436) and 202 nm (ε =22764). A red shift is expected in the spectra if solvent polarity increases.

The first $(\pi,\pi^*)^1$state is composed of one main configuration $\theta_{47}^{-1}\ \theta_{50}$ which is a delocalized band.

The second $(\pi,\pi^*)^1$ state is by far much more polar than the ground state and is also composed of one main band $\theta_{46}^{-1}\theta_{49}$ which is a CT band from Ar_1 to Ar_2 and acrolein. This state is not expected to show any appreciable solvent dependence .

The third $(\pi,\pi^*)^1$ state is composed of two configurations $\theta_{46}^{-1}\theta_{49}$ which is CT band from Ar_1 to Ar_2 and acrolein , $\theta_{48}^{-1}\theta_{50}$ which is a delocalized band.

d- Electronic absorption spectra of 3-(3',4'methylenedioxyphenyl) -1- (4'-methoxy phenyl) –2-propen-1-one (IV)

The spectra of IV in polar and non-polar solvents are presented in Fig. 5. The theoretically computed transitions and their assignment are given in Table 5.The spectra of IV is completely different than any one of the previous derivatives in shapes, intensities and band positions . This may be attributed to the two bulky groups attached to phenyl moiety .

The first ($\pi,\pi^*)^1$ state predicted theoretically at 318 nm . This band observed at 355nm in ethanol and 332nm in cyclohexane . This state possesses a dipole moment slightly greater than that of the ground state . This polar state is composed of one main configuration $\theta_{52}^{-1}\ \theta_{55}$ which is CT from $Ar_1 \rightarrow Ar_2$ and acrolein. As the solvent polarity

increases a red shift is expected . The vibrational structure of the band centered at 305nm in both solvent is not predicted theoretically due to low intensity and low stability.

The second ($\pi,\pi^*)^1$ state predicted theoretically at 263 nm. This band centered at 256 nm in cyclohexane and at 262 nm in ethanol. The polarity of this state is almost the same as the ground state, hence, no solvent dependence is observed. This state is composed of one configuration $\theta_{51}^{-1}\ \theta_{54}$ which is CT from $Ar_2 \rightarrow Ar_1$and acrolein.

The third ($\pi,\pi^*)^1$ state centered at 205 nm in both solvent and predicted theoretically at the same position. No solvent dependence is observed, and this state is composed of two configurations, namely , $\theta_{51}^{-1}\ \theta_{54}$ and $\theta_{53}^{-1}\ \theta_{55}$.

e- Electronic absorption spectra of 3-(3',4'-methylenedioxyphenyl)–1-(4-bromophenyl) –2-propen-1-one (V)

The spectrum of (V) is presented in Fig. 6 in polar as well as in non-polar solvents. The spectrum is composed of two main folds ; The long wavelength centered at 348 nm (ε =32720) in cyclohexane and at 362 nm (ε =27834) in ethanol. The second band centered at 258 nm (ε =24737) in cyclohexane and at 268 nm (ε = 23925) in ethanol.

Table (6) presents the observed and calculated state and their assignment. The first ($\pi,\pi^*)^1$ state is composed of one main configuration $\theta_{49}^{-1}\ \theta_{52}$ which is CT from Ar_1 to Ar_2 and acrolein. This band shows a red shift upon increasing solvent polarity.

The second $(\pi,\pi^*)^1$ state is composed of two configurations, namely, $\theta_{49}^{-1}\theta_{51}$ and $\theta_{50}^{-1}\theta_{52}$. Both are CT from Ar_1 to Ar_2 and acrolein and from Ar_2 to acrolein respectively, and show no solvent dependence on band positions.

The short wavelength predicted at 201 nm agrees with the observed band and is composed of one main configuration $\theta_{50}^{-1}\theta_{51}$ which is CT from Ar_2 to Ar_1 and acrolein and also shows no solvent dependence.

Compound	λ , nm		Є, L .mol^{-1} cm^{-1}	
	Ethanol	Cyclohexane	Ethanol	Cyclohexane
I	308	296	28705	27132
	236	235	15136	12334
	201	201	31526	12844
II	298	283	21485	32230
	235	235	12805	12805
	205	205	32058	30150
III	320	315	34955	36425
	225	225	12436	16723
	202	202	22764	15127
IV	355	332	23426	32720
	306	305	17518	22809
	262	256	14356	15635
	205	205	38625	39722
V	362	348	27834	32416
	268	258	23925	24737
	201	201	39815	39926

Table (1) : Observed wavelengths and molar extinction coefficient for the studied compounds in ethanol and cyclohexane .

State	Config.	Assignment	Δ E, eV	
			Observed	Calcld.
I	$\theta_{38}^{-1}\ \theta_{41}$	CT $Ar_1 \rightarrow Ar_2$ + acrolein (π , π *)	4.0260	4.1212
II	$\theta_{38}^{-1}\ \theta_{40}$	CT $Ar_1 \rightarrow$ acrolein $+Ar_2$ (π , π *)	5.2542	4.9869
	$\theta_{37}^{-1}\ \theta_{40}$	CT $Ar_1 \rightarrow$ acrolein $+Ar_2$ (π , π *)		
III	$\theta_{37}^{-1}\ \theta_{40}$	CT $Ar_1 \rightarrow$ acrolein $+Ar_2$ (π , π *)	6.1386	6.0712
	$\theta_{39}^{-1}\ \theta_{41}$	CT acrolein $\rightarrow$ Ar_2 (π , π *)		

Table (2) : State function ,configuration and assignment for trans-(s-cis)-1,3- diphenyl - 2-propen-1-one (I) .

State	Config.	Assignment	Δ E, eV Observed	Calcld.
I	$\theta_{41}^{-1}\ \theta_{44}$	CT $Ar_2 \rightarrow Ar_1$ + acrolein (π , π *)	4.1610	4.1840
II	$\theta_{41}^{-1}\ \theta_{43}$	CT $Ar_2 \rightarrow$ acrolein $+Ar_1$ (π , π *)	5.2766	4.9869
	$\theta_{42}^{-1}\ \theta_{44}$	CT Ar_2 + acrolein $\rightarrow +Ar_1$ (π , π *)		
	$\theta_{40}^{-1}\theta_{43}$	CT $Ar_1 \rightarrow$ acrolein (π , π *)		
III	$\theta_{40}^{-1}\theta_{43}$	CT $Ar_1 \rightarrow$ acrolein (π , π *)	6.0487	6.2976

Table (3) : State function,configuration and assignment for 1-phenyl -3-(3 -tolyl)-2-propen-1-one (II).

State	Config.	Assignment	Δ E,eV Observed	Calcld.
I	$\theta_{47}^{-1}\ \theta_{50}$	Delocalized band	3.8750	4.0705
II	$\theta_{46}^{-1}\ \theta_{49}$	CT $Ar_1 \rightarrow Ar_2$ + acrolein (π , π *)	5.5111	4.9731
III	$\theta_{46}^{-1}\ \theta_{49}$	CT $Ar_1 \rightarrow Ar_2$ acrolein (π , π *)		
	$\theta_{48}^{-1}\ \theta_{50}$	Delocalized band	6.1386	5.8165

Table (4) : State function , configuration and assignment for 3-(4-bromo- phenyl) – 1- (4-methoxyphenyl)–2-propen-1-one (III)

State	Config.	Assignment	Δ E, eV Observed	Calcld.
I	$\theta_{52}^{-1}\ \theta_{55}$	CT $Ar_1 \rightarrow Ar_2$ + acrolein (π , π *)	3.4930	3.8962
II	$\theta_{52}^{-1}\ \theta_{54}$	CT $Ar_1 \rightarrow Ar_2$ + acrolein (π , π *)	4.7328	4.7094
III	$\theta_{53}^{-1}\ \theta_{55}$	CT $Ar_2 \rightarrow Ar_1$ + acrolein (π , π *)	6.0488	5.8222
	$\theta_{51}^{-1}\ \theta_{54}$	CT $Ar_2 \rightarrow Ar_1$ + acrolein (π , π *)		

Table (5) : State function,configuration and assignment for 3-(3-,4-methylene- dioxy phenyl)-1-(4- methoxy phenyl)–2-propen-1-one (IV) .

State	Config.	Assignment	Δ E,eV Observed	Calcld.
I	$\theta_{49}^{-1}\ \theta_{52}$	CT $Ar_1 \rightarrow Ar_2$ + acrolein (π , π *)	3.4254	3.9829
II	$\theta_{49}^{-1}\ \theta_{51}$	CT $Ar_1 \rightarrow Ar_2$ + acrolein (π , π *)	4.6269	4.6570
	$\theta_{50}^{-1}\ \theta_{52}$	CT $Ar_2 \rightarrow$ acrolein (π , π *)		
III	$\theta_{50}^{-1}\ \theta_{51}$	CT $Ar_2 \rightarrow Ar_1$ + acrolein (π , π *)	6.1692	6.4556

Table (6) : State function,configuration and assignment
for 3-(3-,4-methylene dioxy phenyl)–1-(4- bromo phenyl)–2-propen-1- one (V) .

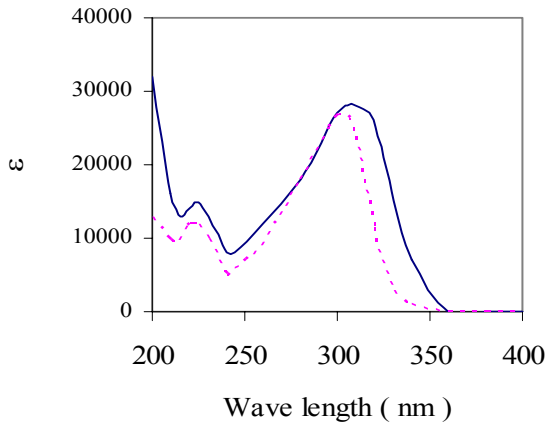
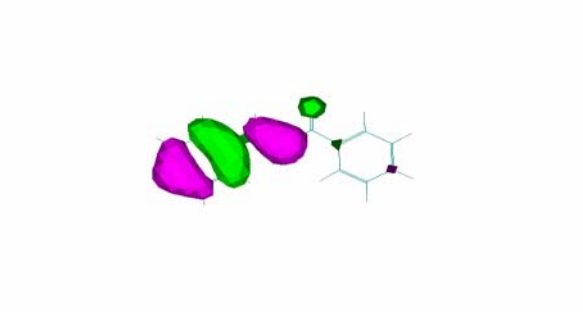
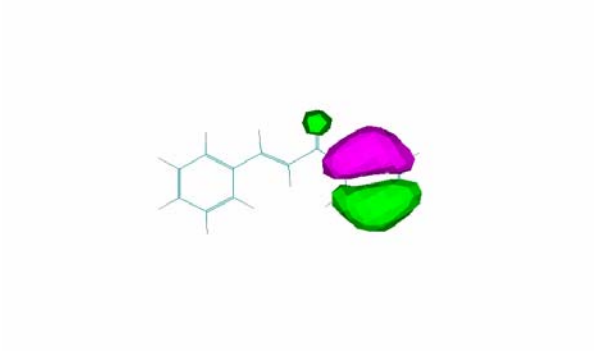


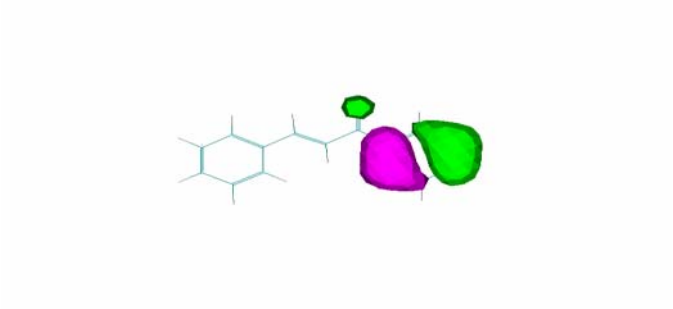
Fig.1 : Absorption spectra of (I) in ethanol (—) , in cyclohexane (….) .



Ψ_{39}

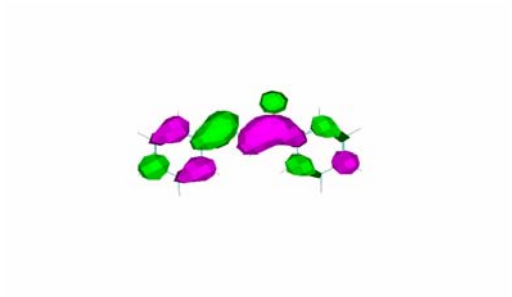


Ψ_{38}

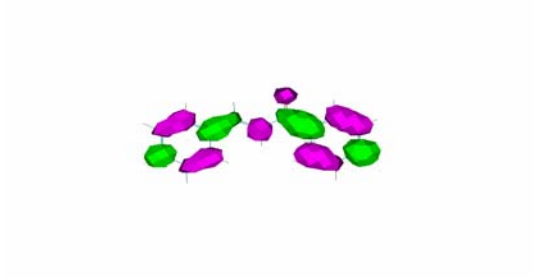


Ψ_{37}

Fig. 2a : Charge density maps of the three occupied MO's considered in the transition for 1,3–diphenyl–2–propen–1–one .



Ψ_{40}



Ψ_{41}

Fig.2b : Charge density maps of the two vacant MO's considered in the transition for 1,3-diphenyl–2–propen–1–one .

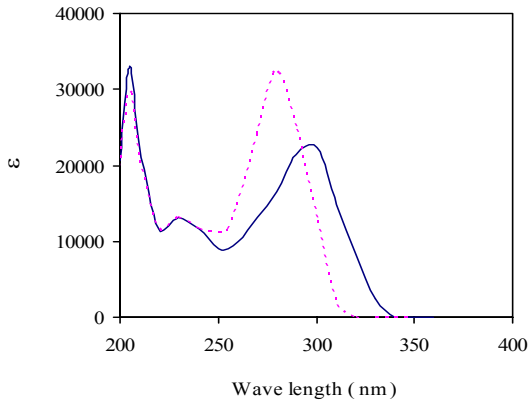


Fig.3 : Absorption spectra of (II) in ethanol (—) , in cyclohexane (.....) .

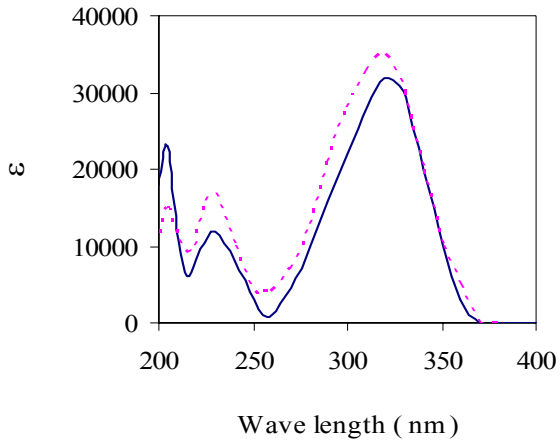


Fig. 4 : Absorption spectra of (III) in ethanol (—) , in cyclohexane (….) .

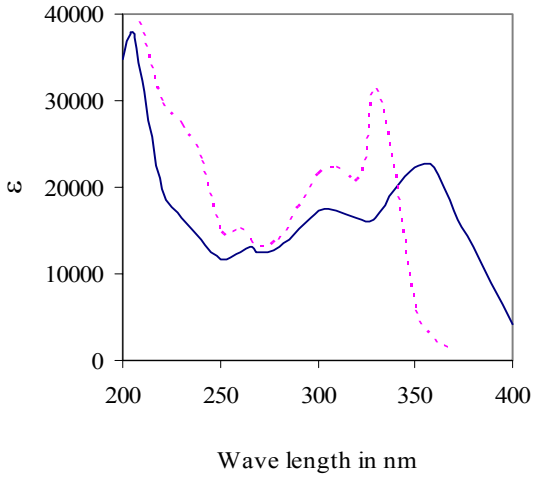


Fig. 5 : Absorption spectra of (IV) in ethanol (—) , in cyclohexane (…..) .

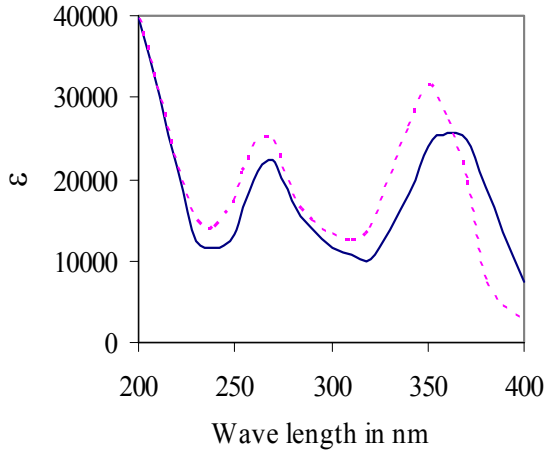


Fig. 6 : Absorption spectra of (V) in ethanol (—) , in cyclohexane (…..) .

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