CONFORMATIONAL INVESTIGATION OF THE ELECTRONIC STRUCTURE AND SPECTRA OF SOME HETEROCYCLIC BENZOYL COMPOUNDS

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The electronic structures and molecular conformations of pyridyl-, 2-furyl- and 2-thienylphenylketones have been investigated experimentally by the electronic absorption spectra and theoretically with Density functional Theory (DFT) and time dependent density functional theory (TDDFT). The observed transitions were identified and assigned to be $n - \pi^*$, $\pi - \pi^*$ or charge transfer (CT) one. The optimized conformers for the studied compounds have been found to be the cis-planar conformers. Molecular orbital calculations confirmed the linear conjugation for the studied molecules.

1- Introduction

Qualitative and quantitative investigations of the electronic spectra of the large organic molecules are a subject of interest [1] . The issue of cross- and linear conjugation can be discussed for compounds, which involve subsystems, such as the pyridyl, 2-furyl- and 2-thienlphenyl-ketones through the investigation of their electronic spectra.

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The electronic spectra of benzoyl derivatives of oxygen and sulphur- containing heterocyclic together with Huckel MO calculations have been investigated[2]. The excitation energies of the maxima of the first bands in the electronic absorption spectra were in a linear correlation with the calculated $N \rightarrow V_1$ transition energies.

Investigation of torsion angles resulting from steric hindrance[5] and dipole moment measurement[4] indicated that for 2-thienylphenylketone, the conjugation of the 2-thienyl, carbonyl and phenyl groups tends to confirm a planar structure and its conformer is the cis conformer. Kaper et al[5] studied, qualitatively, the conformation of 2-furyl- and 2-thienylphenylketone through their electronic spectra. They concluded that the conjugation between the heterocyclic ring and the carbonyl group was superior and the phenyl ring has turned out of the plane of the heterocyclic and carbonyl group.

The time-dependent density functional theory (TDDFT) is well known as a rigorous formalism for the treatment of transition energies within the DFT framework. The combination of efficiencies, that is, computational cost and precision, makes TDDFT attractive[6]. Excited states can be modeled in the presence of solvents using the TDDFT method[7].

The aim of this work is to investigate the electronic structure and extent of interaction between various subsystems of the studied compounds to confirm the type of interaction between subsystems. Quantitative and qualitative interpretations of the electronic spectra of the studied molecules are presented.

2- Computational Methods

All calculations have been performed using the GAUSSIAN03 package[8]. Ground-state geometries have been obtained at Density Functional Theory (DFT) level using Becke's three parameter

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hybrid exchange functional and the Lee-Yang-Parr correlation functional[9] (B3LYP) with the 6-31G(d) basis set level of the theory. Electron excitation energies related to the absorption spectra were calculated using the time-dependent density functional response theory (TDDFT)[10] with the 6-31G(d) basis set. To estimate the effects of the polar solvent, self-consistent reaction field (SCRF) calculations were carried out using a polarized continuum model (PCM)[11].

3- Results and Discussions

A- The Electronic Absorption Spectra
a- Pyridylphenylketones

The electronic absorption spectra of 2-pyridyl-, 3-pyridyl- and 4-pyridylphenylketones in ethanol are given in Figure 1. The spectra show two main bands in the region 400-330 nm and 300-230 nm. The 4-pyridyl derivative shows an additional band at 221nm. The first band region (400-330 nm) can be safely assigned to $n - \pi^*$ transitions (Figure 1), as reflected by its low intensity (210, 450 and 150 l mole^{-1} cm^{-1} for 2-, 3- and 4-pyridyl derivatives respectively).

Gaussian analysis for the second band, 300-230 nm, indicates existence of four transitions beside a fifth transition occures in the region 230-220 nm. These transitions are assigned to $\pi - \pi^*$ or CT transitions as indicated by their high intensities (Table 1).

It has been shown previously[12] that the π- conjugation in ketone, as those studied compounds, is a cross conjugation. The type of conjugation can be predicted experimentally and theoretically. Experimentally, one compares the electronic spectrum of the studied ketone with those of pyridine aldehyde and benzaldehyde. The similarity, in positions of band maxima, between the spectrum of the

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ketone and the specific aldehyde indicates the type of conjugation whether it is over benzoyl or pyridoyl subsystems.

A comparison between the spectra in Figure 1, of the studied ketones, and Figure 2 of the aldehydes is very interesting. The similarity between the spectra of any of the specific aldehyde and the studied ketones is missing. This result indicates that conjugation over the studied ketones is linear and not cross one. A confirmation of this conclusion will be verified by the results of molecular orbital calculations.

b- 2-Furyl and 2-thientlphenylketones
Figure 3 shows the absorption spectra of 2-furylphenylketone and 2-acetylfuran, for comparison. Very important results can be reflected from the comparison between the observed spectra. The spectrum of 2-acetylfuran is totally different from that of furan[13]. This result indicates the coplanar of the furan ring and the carbonyl chromophore which, in turn, maximizes the π-cojugation and electron delocalization overall the system.

The spectrum of 2-furylphenylketone shows a broad intense band with a maximum around 290 nm, which overlaps at its short wavelength end with a broad intense shoulder (around 260 nm). A distinct feature of the spectrum of this ketone is that its not the additive spectra of furan plus benzaldehyde or of benzene and furanaldehyde. This observation indicates that the molecule is planar and π-conjugation is maximum. This conclusion is only attended at a situation of linear, not cross, conjugation. Thus one has, at hand, an experimental evidence for the coplanar of such molecule.

To confirm the above evidence, planarity as well as the linear-conjugation of the molecule, one studied the electronic spectra of 2-thienylphenylketone and 2-acetylthiophene in ethanol (Figure 4).The spectrum of 2-thienylphenylketone, shows two distinct intense and highly overlapping transitions in the 310-230 nm region.

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A close investigation of the spectrum of 2-acetylthiophene are the same specially concerning the position of band maxima. This behavior was not observed neither in the case of 2-furylphenylketone nor in the case of 2-pyridylphenylketone. One expected the same or nearly the same conformer for the three studied ketones but spectral observations show that this is not the situation. Similarity in the spectral behavior for the studied compounds is in the results of Gaussian analysis which gives five transitions (Ttable 1).

The spectrum of 2-thienylphenylketone is directed to the presence of cross-conjugation in spite of the absence of band correspond to benzene transition in the spectrum. This observation and big difference in intensity of transitions of both 2-thienylphenylketone and 2-acetylthiophene let the experimental evidence for cross-conjugation is not satisfied or enough. Molecular orbital calculation for the spectra is required for all the studied compounds to get more evidences for the correct conformers.

B- Molecular orbital Treatment

Optimized ground – state geometry of the studied compounds depicted in figure 5 shows that the molecular framework is planar, all atoms are lying in one plane. The transition energies for the studied compounds are calculated for the optimized conformer in the gas phase and with ethanol as solvent.

A very good agreement between the calculated and experimental transitions which confirm that the conjugation of the studied molecules is linear is shown in Table 1. Also, the quantitative interpretation of the electronic spectra through molecular orbital computations not only confirm the linear conjugation phenomena for these compounds but it helps in assigning the electronic transitions as $n - \pi^*$, $\pi - \pi^*$ or CT transition.

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A comparison between the calculations for gas phase and for solution using ethanol as polar solvent helps in assigning the transitions (Table 1). The occurrence of red shift in the transition due to increasing polarity indicates that the nature of transition is charge transfer one· (CT). Calculations for all the studied compounds showed the absence for the planarity of the studied molecules.

4- Summary

The optimized geometries of the studied compounds were calculated at DFT level by employing B3LYP with 6-31G(d) basis sets. TDDFT has been used to determine the transition energies. Self-consistent reaction field (SCRF) calculations were carried out using a polarized continuum model (PCM) to estimate the effect of polar solvent. Geometry optimization indicates that the studied compounds are planar. The π - conjugation in the studied compounds is planar and calculations showed the absence of localized transition which is an evidence for the planarity of the studied molecules.

Table 1 : Experimental transitions energy (E_{exp}), molar extinction coefficients (ε), theoretical transitions energy (E_{calc}) in gas and solvent and assignment of bands for the studied compounds.

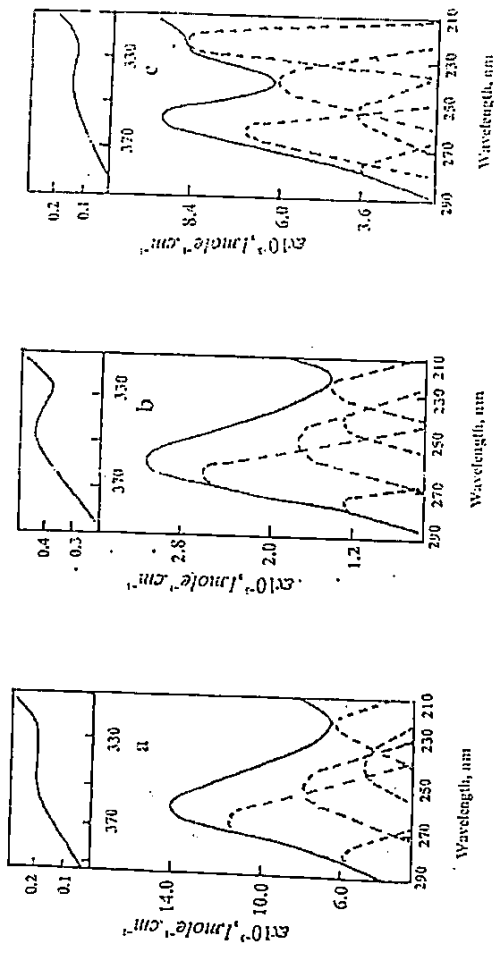| Compounds	Observed transitions eV (E_{exp})	Molar extinctions coefficient $\varepsilon x 10^{-3}$	Calculated transitions (E_{calc}) Solvent	Gas phase	Assignments
2-pyridyl-phenylketone	3.65	0.00	3.59	3.45	
	4.39	5.80	4.39	4.61	$n \rightarrow \pi^*$
	4.67	11.30	4.61	4.81	CT
	5.00	7.70	4.81	4.86	CT
	5.19	4.50	5.12	4.96	$\pi \rightarrow \pi^*$
	5.55	6.50	5.37	5.28	$\pi \rightarrow \pi^*$
					$\pi \rightarrow \pi^*$
3-pyridyl-phenylketone	3.59	0.00	3.61	3.49	
	4.43	1.25	4.42	4.56	$n \rightarrow \pi^*$
	4.67	2.56	4.58	4.73	CT
	4.98	1.72	4.89	4.76	CT
	5.14	1.25	4.92	4.96	$\pi \rightarrow \pi^*$
	5.50	1.39	5.39	5.28	$\pi \rightarrow \pi^*$
					$\pi \rightarrow \pi^*$
4-pyridyl-phenylketone	3.21	0.00	3.58	3.49	
	4.44	3.46	4.33	4.45	$n \rightarrow \pi^*$
	4.75	7.00	4.50	4.58	$\pi \rightarrow \pi^*$
	4.89	3.60	4.55	4.68	CT
	5.19	6.00	5.29	5.15	CT
	5.61	8.70	5.40	5.35	$\pi \rightarrow \pi^*$
					$\pi \rightarrow \pi^*$
2-furyl-phenylketone	4.30	16.10	4.29	4.47	CT
	4.54	3.60	4.45	4.61	CT
	4.77	8.90	4.78	4.92	CT
	5.32	3.90	5.44	5.55	CT
	5.61	2.50	5.68	5.57	$\pi \rightarrow \pi^*$

Figure 1: Electronic absorption spectra in ethanol for:
a- 2-pyridylphenylketone; _____ overall, _____ deconvoluted.
b- 3-pyridylphenylketone; _____ overall, _____ deconvoluted.
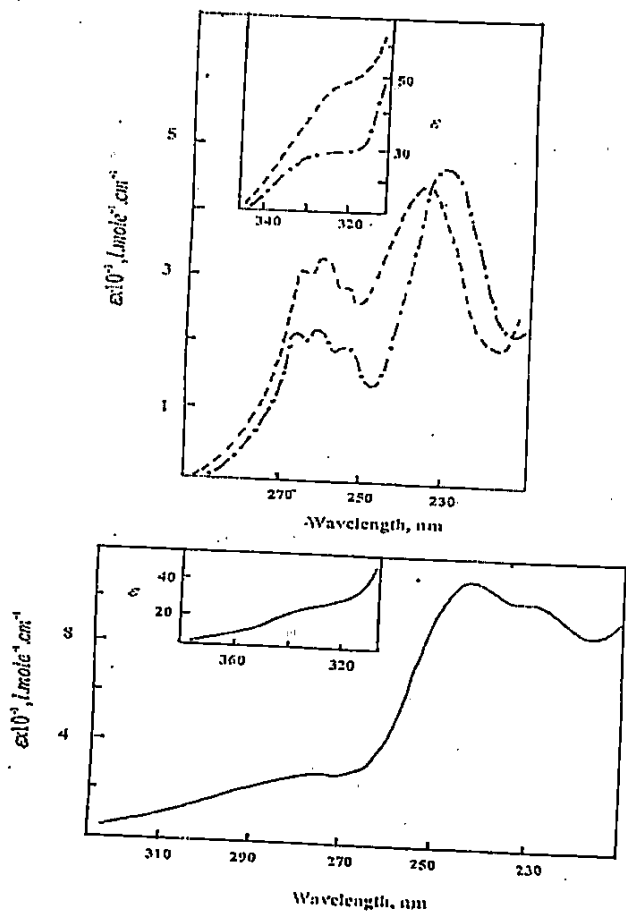c- 4-pyridylphenylketone; _____ overall, _____ deconvoluted.

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Figure 2: Electronic absorption spectra in ethanol for:
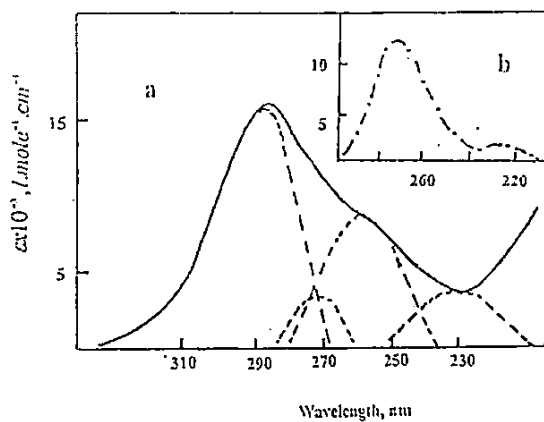——— benzaldehyde, ——— 2-pyridine aldehyde, ·········· 3-pyridine aldehyde

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Figure 3: Electronic absorption spectra in ethanol for:
a- furylphenylketone; _____ overall, ------------- deconvoluted.
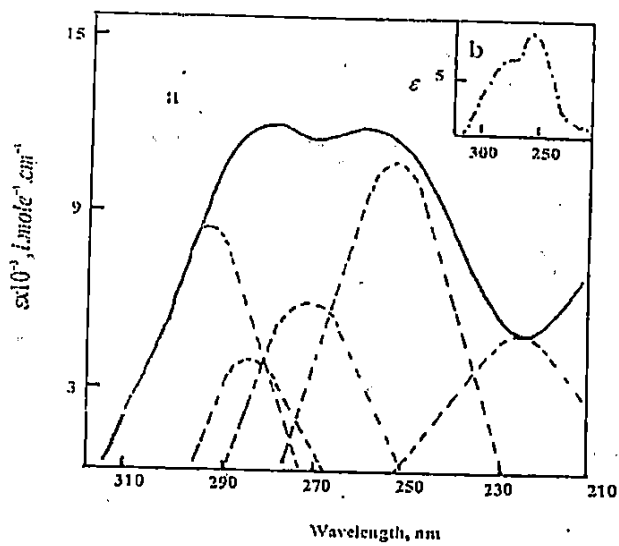b- 2-acetylfuran ·-·-·-·-·-·-

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Figure 4: Electronic absorption spectra in ethanol for:
    a-　2-thienylphenylketone; _____ overall, ------------- deconvoluted
    b-　2-acetylthiophene -.-.-.-.-.-.

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دراسة التركيب الإلكترونى والطيفي لبعض مركبات البنزويل

محمد عبده

تم عملياً ونظرياً دراسة التركيب الإلكتروني والشكل الفراغي للمواد المدروسة ، وتم تحديد نوعية الانتقالات الإلكترونية . ثبت أن شكل المركبات فى الفراغ فى مستوى منبسط .

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