Spectroscopic Studies of Electron Donor-Acceptor Chromogens of Oxazolin-5-one Derivatives.

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Abstract:

The electronic absorption spectra of some electron donor-acceptor (EDA) chromogens of oxazolin-5-one derivatives showed marked sensitivity towards number of organic solvents of different polarity. It is deduced that in (HBD-A) solvents, hydrogen bonding is responsible for the negative solvatochromic behaviour by forming H-bonding complexes in the ground state, leading to increase ECT as H-bonding abilities of the solvent increases $\propto$-value. In (HBA) solvents the correlation between ECT and the solvent parameters S_T and Z-values is straight forward. The absorption spectra of 4-N,N-dimethylcinnamylmethylene derivative in ethyl acetate-methanol mixture was discussed. The pka values of some derivatives were determined. The mass spectrum of 4-N,N-dimethylcinnamylmethylene derivative was studied at different temperatures. Biological activity was also studied where the compounds containing the substituents $(CH_3)_2NC_6H_4-$ and $CH_3OC_6H_4-$ gave +ve results on all tested organisms.

Introduction:

A broad class of dyestuffs are based on electron donor acceptor chromogens, such compounds have found many applications, such as in dyeing of fabric, colouring of toners and in image forming and optical information storage technologies [1-4] However, little attention has been given to the electronic structure of oxazolin-5-one compounds, this prompted to predict and control the properties of those dyes. The present work is thus focused on the role of solvents in controlling the intramolecular charge transfer (ICT) process for electron donor acceptor (EDA) dye molecules [5-11] which have the same acceptor group with different electron donor moieties. Moreover, medium effect and mass spectra as well as biological activity of these compounds.

Experimental:

[4-(4-Arylmethylene)-2-(4-nitrophenyl)] oxazolin-5-ones I-IV were prepared [12].

The used solvents were purified according to Vogel [13a] and Or-
ganicum [13b]. The UV-VIS absorption spectra were recorded on a Perkin-
Elmer 555UV spectrophotometer. Buffer solutions were prepared as recom-
menended by Britton and Robinson [14]. The mass spectra were measured on
Shimadzu, GC MS-QP 1000EX Gas chromatograph. Mass spectrometer (electron
impact ionization 70ev, temperature ion source 200 C^o and mass resolution
1000). Least square analysis was used.

Ar:

I - 4- $Me_2N- C_6H_4-CH=CH-$
II - 4- $Me_2N-C_6H_4-$
III- 4- $MeO- C_6H_4-$
IV - 4- $HO- C_6H_4-$

$Ar - CH = C --- C = O$
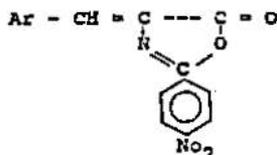
Results and Discussion:

1- UV-VIS Spectra

i- Band assignment

The UV spectra of the investigated compounds were measured in
methanol and n-hexane. The spectra display mainly two groups of bands,
the first group at 210 and 213 nm (in methanol and n-hexane respec-
tively) which can be assigned to $\pi - \pi^*$ transition of 2-p-nitro aromatic
ring. The second group of bands are within 252-255nm range in methanol
and within 245 - 253nm range in n-hexane indicating $\pi - \pi^*$ transition of
4-p-substituted aromatic ring.

ii - Solvent effect

The present work is dealing with the changes in the spectra of
compounds I-IV which accompanied variation of solvent polarity,
(cf.Tables 1,2). The data demonstrate that in amphiprotic solvents
(HBD-A), as the polarity of the solvent increases (relative to E_T
value[15],Z-value [16], dielectric constant[17] and $\propto$-value[18a]), the
transition energy of the compounds I-IV increases. This may be at-
tributed to the fact that the charge separation between the donor groups
($-N(CH_3)_2$,$-OCH_3$,$-OH$) and the carbonyl group as acceptor is greater in
the ground state than that in the excited state. This indicate that the

-116-

2

polarity of the solvents play an important role in stabilizing the ground state through dipole-dipole or dipole-induced dipole interactions[4,19,20]. The above results provide good evidence that hydrogen bond (HB) specific interaction dominates the overall solvent effect in this class of solvents, in other words, HB donor strength i.e α-value is largely responsible for the blue shift. On the other hand, compounds I-III display a red shift in basic oxygenated solvents (HBA) which is due to hydrogen bonding acceptor strength of these solvents i.e β-value[18b], so destabilization of the ground state of the molecule and consequently decreases its electronic transition energy. Compounds I-III demonstrate bathochromic shift in non-hydrogen bonding solvents (NHB) which is attributed to the change in the structures from non-polar state to polymethine state [21].

However it is obvious that there is no correlation between compound IV and the polarity of (HBA and NHB) solvents since these solvents may form complexes with the oxazolone ring and not with the conjugated donor-acceptor system.

It is worth noting that compounds II, III, IV show shoulders in (NHB) solvents or maximum splitting to give two maxima specially compound II in cyclo- and n-hexane. This may be attributed to the electron promotion from two orbitals of the donating group to the same or different orbitals [22,23] of the acceptor part.

Attempted correlation between ECT and solvent polarity parameters (E_T, π-, α), were successful. Strong deviation was observed in case of alcoholic solvents relative to the non alcoholic ones (HBA and NHB), this deviation is attributed to strong interaction between these alcoholic solvents and the investigated compounds I-IV (cf. Table 3).

In conclusion, the results demonstrate the existence of $\pi - \pi^*$ and $n - \pi^*$ transitions which are responsible for intramolecular charge transfer of the non bonding electrons of the donating groups ($-N(CH_3)_2$, $-OCH_3$, $-OH$) to the acceptor part of the molecule. There is a successful correlation between some solvent polarity parameters and the investigated compounds. H-bonding is responsible for the blue shift in (HBD-A) class indicating that UV-VIS spectra is largely dependent on the kind of solvent.

-117-

3

iii- Spectra of mixed solvents :

It is of interest to investigate the characteristic behaviour of compound I in ethyl acetate-methanol mixture, where a hypochromic and red shifts is observed due to gradual formation of intermolecular hydrogen bonded solvated complex between compound I and the relatively acidic methanol (α -value) which added with successively increased quantities to ethyl acetate as a basic solvent (HBA). An isosbestic point exists around 423 nm suggesting presence of an acid-base equilibrium in such medium, $HL + H \leftrightharpoons H_2L$. It is evident that in ethyl acetate the molecule exists in basic form HL where with increasing the amount of methanol the donor portion increases in the medium consequently increasing the acidic form H_2L accompanied with red and hypochromic shifts. This is consistent with the explanation that the electronic transition (λmax) in this molecule is due to intramolecular CT which showes high sensitivity to medium properties. The equilibrium constant is calculated according to the following equation [24].

$$\frac{[A][D]}{d} = \frac{[D]}{\mathcal{E}_c} + \frac{1}{k\,\mathcal{E}_c}$$

Where [D] is donor quantities ranging from 0.0% to 6%, [A] is acceptor quantity, d is absorbance at λmax, $\mathcal{E}_c$ is the molar absorptivity of the complex. The plot of [A][D]/d value against [D] is linear. From the slope and intercept the value of k is calculated and found to be 1.02 $L.mol^{-1}$.

iv - Spectra in buffer solutions

The spectra of compounds I and II were recorded in buffer solutions (50% E_tOH v/v). A clear isosbestic points at 458nm and 410nm for compounds I and II respectively are observed indicating a simple protolytic equilibrium between MH^+ (protonated compound) and M species. $M + H^+ \leftrightharpoons MH^+$ where MH^+ is a short wavelength species whose lone pair of nitrogen electrons is blocked due to acceptance of proton from the medium, so decreasing the intramolecular CT. The pKa values were found to be 1.85 for compound I and 1.42 for compound II indicating that compound 1 is more basic than II.

-118-

4

2- Mass spectra

The mass spectrum of compound II was carried out at different temperatures below m.p (Direct Inlet Prob 95,120, 145 and 200 C^0). It gives the moleculer ion peaks at m/z=337 and base peaks at m/z=195 at all investigated temperatures. (Table 4) showes that with increasing, the temperature from 95 to 200 C^0 the half life time of the ions decrease.

Also 120 C^0 is the optimum temperature at which all fragments are relatively more stable and exist. It is worth noting that the molecule is fragmented according to four pathways A,B,C and D. The ion m/z=145 is the common product of the four pathways (cf. Chart 1).

3 - Biological activity :

The investigated compounds were screened for antibacterial activity against Escherichia coli, Pseudomonas flourescence, Bacillus cerious, Bacillus subtilis. Aspergillus niger and Penicillium cyclopium at concentrations of 800,500,100 and 50 ppm. These compounds were also screened for antifungal activity at the same concentrations[25]. The results are shown in (Table 5). It was found that compounds II and III are the most effective on all tested organisms, where compound I and IV were found to be not effective.

5

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دراسات طيفيه لبعض مشتقات اوكزازولين ٥٠-١ ون
ذات مجموعات معطيه ومكتسبه للالكترون

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الملخص العربى

حفرت بعض مشتقات الاوكزازولين ٥٠-١ون وتم دراسة الطيال
الامتصاص الالكترونية فى المزيبات العضوية ذات القطبيه المختلفة
وذلك فى منطقة الطيف المرئى والاشعة فوق البنفسجية . كذلك تم دراسة
طيف الامتصاص   لبعض المشتقات المحتوى على $N(CH_3)_2-$ فى
محاليل مائية ذات ارقام هيدروجينية مختلفة وقد تم حساب ثابت
الاتزان. كذلك تم حساب ثابت الاتزان عند دراسة طيف الامتصاص لبعض
هذه المشتقات فى مخلوط من مزيبين احدهما له خواص حمضيه والاخر له
خواص قاعدية. بالاضافة الى ذلك تم دراسة طيف الكتله عند درجات
الحرارة المختلفه وايضا التاثير السيرلوجى لهذه المركبات على بعض
انواع من البكتريا والفطاب.

Table (1): Effect of Solvents on Compounds I and II in Different Classes of Solvents :

Solvent	ET (K.cal mol)-1	Z	ω	B	Dielectric constant at 20 c°	λ_{max} (n m) I	II	Transition energy (ev) I	II	ε_{max} L.sol-1.cm-1 I	II	$\Delta\bar{\nu}_{1/2}$ cm-1 I	II
Gp.-A :													
MeOH	55.5	83.6	0.90		32.6	527	498	2.352	2.409	25914	45436	4182	3698
EtOH	51.9	79.6	0.850		24.3	532	498	2.330	2.389	31561	43831	4033	3670
iso-ProH	48.9	76.3	0.657		18.3	535	503	2.317	2.465	25611	40822	4003	3751
IPA													
DMSO	45.0	71.1		0.752	46.9	545	512	2.275	2.421	26479	42040	3755	3724
DMF	43.8	69.5		0.710	36.7	539	507	2.300	2.445	27341	36721	3970	3204
Acetone	42.2	65.7		0.719	20.7	526	495	2.357	2.505	31372	44066	4126	3731
Ethyl acetate	39.1	59.4		0.601	6.0	519	490	2.389	2.530	36805	34704	4387	3631
Dioxan	36.0	--		0.363	2.2	517	489	2.390	2.540	37208	36960	4040	3577
MIU													
CH2Cl2	41.1	64.2			8.9	542	507	2.287	2.445	26217	32317	3567	3539
Benzene	34.5	--			2.3	530	495	2.339	2.505	28125	39568	3611	3426
Toluene	33.9	--			2.4	528	494	2.349	2.516	33760	40621	3900	3525
CCl4	32.5	--			2.2	520	481, 502 sh	2.384	2.577	35040	38014	3762	3042
Cyclohexane	31.2	--			2.0	556	468*	2.450	2.649	32772	39618	3566	2975
n-Hexane	30.9	--		1.9		500	494, 464*, 487	2.480	2.672	17898	30311	4641	3532

* Two Maxima.

Table (2): Effect of Solvents on Compounds III and IV in Different Classes of Solvents.

Solvent	ET K.cal mol⁻¹	Z	α	b	Dielectric constant at 20 c°	λmax (n s) III	IV	Transition energy (ev) III	IV	εmax L.mol⁻¹.cm⁻¹ III	IV	Δν₁/₂ cm⁻¹ III	IV
HO – A.i													
MeOH	55.5	93.6	0.09		32.6	403	375	3.078	3.306	29000	26909	4416	4612
EtOH	51.9	79.6	0.650		24.3	405	377	3.061	3.289	33100	28163	4321	4688
iso-PrOH	48.9	76.3	0.687		18.3	406	379	3.054	3.271	28028	30232	4201	4880
HA													
DMSO	45.0	71.1	0.752		46.9	412	395	3.009	3.139	32321	27046	4538	4923
DMF	43.8	69.5	0.710		36.7	409	380	3.031	3.263	30705	18044	4656	1799
Acetone	42.2	65.7	0.499		20.7	404	376	3.069	3.297	34291	29073	4543	4955
Ethyl acetate	38.1	59.4	0.401		6.0	403	377	3.076	3.269	43750	31957	4367	4955
Dioxan	36.0	--	0.363		2.2	403 366 sh	378 366 sh	3.076	3.250	41200	30296	4206	4609
HB													
CH2Cl2	41.1	64.2			8.9	412 393 sh	383 368 sh	3.009	3.237	37650	19778	4533	3609
Benzene	34.5				2.3	410	386 370 sh	3.024	3.212	39750	27075	4359	4499
Toluene	33.9	--			2.4	409	386 369 sh	3.031	3.212	41750	31202	3920	4931
CCl4	32.5				2.2	409	367 370 sh	3.031	3.204	40750	30699	3834	2752
Cyclohexane	31.2	--			2.0	405 434 sh 427 sh	384 370 sh 367 sh	3.061	3.220	46250	30951	3169	2025
n-Hexane	30.9	--			1.9	401 422 sh 402 sh	380 363 sh 356 sh	3.092	3.263	46250	30951	3387	3753

Table (3) : The linear interrelation between Transition Energy Eet (ev) and Solvent Parameters for Compounds I-IV.

Compound	Linear equation	Solvent	X	Y	Linear equation	Solvent	X	Y
			Z	Eet (ev)			Z	Eet (ev)
I	$y=1.515 \times 10^{-1} X + 1.949$ $\rho=0.9955$	MeOH,EtOH,Iso-PrOH			$y=5.330 \times 10^{-3} X + 2.955$ $\rho=0.9955$	MeOH,EtOH,Iso-PrOH	ET	Eet(ev)
II	$y=3.153 \times 10^{-3} X + 2.228$ $\rho=0.8371$				$y=3.517 \times 10^{-3} X + 2.299$ $\rho=0.9396$			
III	$y=3.049 \times 10^{-3} X + 2.521$ $\rho=0.9955$				$y=3.360 \times 10^{-3} X + 2.659$ $\rho=0.8901$			
IV	$y=4.776 \times 10^{-3} X + 2.507$ $\rho=0.9974$				$y=5.264 \times 10^{-3} X + 3.013$ $\rho=0.8976$			
I	$y=1.025 \times 10^{-2} X + 2.990$ $\rho=0.9053$	DMSO,DMF,Acetone, ethyl acetate	Z	Eet (ev)	$y=1.630 \times 10^{-2} X + 3.027$ $\rho=0.9955$	DMSO,DMF,Acetone, Ethyl acetate	ET	Eet(ev)
II	$y=-9.934 \times 10^{-3} X + 3.106$ $\rho=0.9031$				$y=1.562 \times 10^{-2} X + 3.136$ $\rho=0.9537$			
III	$y=-5.691 \times 10^{-3} X + 3.122$ $\rho=0.5911$				$y=5.220 \times 10^{-3} X + 3.430$ $\rho=0.9259$			
IV	$y=-1.600 \times 10^{-2} X + 3.949$ $\rho=-0.7251$				$y=1.651 \times 10^{-2} X + 3.995$ $\rho=-0.6769$			
I	$y=0.115 \ X + 2.230$ $\rho=0.9514$	MeOH,EtOH,Iso-PrOH	ET	Eet (ev)	$y=3.810 \times 10^{-2} X + 3.645$ $\rho=0.9749$	Benzene,Toluene, CCl4,Cyclohexane,	ET	Eet(ev)
II	$y=0.0511 \ X + 2.113$ $\rho=0.8871$				$y=4.785 \times 10^{-2} X + 4.143$ $\rho=0.9903$	n-Hexane		
III	$y=0.0715 \ X + 3.003$ $\rho=0.9037$				$y=1.585 \times 10^{-2} X + 3.558$ $\rho=-0.6736$			
IV	$y=0.115 \ X + 3.152$ $\rho=0.9906$				$y=1.090 \times 10^{-2} X + 3.576$ $\rho=-0.7281$			

DMSO - Dimethylsulfoxide
DMF - Dimethylformamide
ρ - Correlation coefficient

Table (4):

m/z	% Relative abundance at			
	95 C	120 C	145 C	200 C
337	24.2	18.2	18.2	17.3
307	--	8.3	2.0	--
267	--	31.9	--	--
189	--	6.1	--	--
188	--	37.2	--	--
187	--	6.6	--	--
159	100	100	100	100
150	--	3.6	2.2	2.5
149	--	4.3	0.4	--
145	--	3.2	2.3	0.8
124	--	14.8	--	--
120	52.4	43.1	10.2	--
92	9.7	8.8	2.7	1.5

Table (5) : Biological Effect of Compounds I-IV on Colonial Growth

Compound	Concentration ppm	Inhibition Zone (diameter) mm					
		Escherichia coli	Pseudomonas flourescence	Bacillus cereus	Bacillus subtilis	Aspergillus niger	Penicillium cyclopium
II	600	20	26	10	19	20	14
	500	8	12	0	6	8	6
	100	8	0	0	0	0	0
	50	0	0	0	0	0	0
III	600	15	32	20	18	26	30
	500	9	20	8	5	7	12
	100	0	8	0	0	0	2
	50	0	0	0	0	0	0

Chart : 1