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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 ∝-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. Biolcgical 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- ons compounds, this prompted to predict and control the properties of these 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.

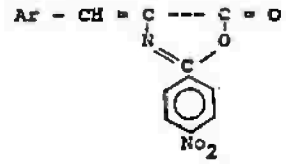
Experimental:

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

The used solvents were purified according to Vogel [13a] and Organicum [13b]. The UV-VIS absorption spectra were recorded on a Perkin-Elmer 555UV spectrophotometer. Buffer solutions were prepared as recommenended 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°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-



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 respectively) 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 α-value[18a]), the transition energy of the compounds I-IV increases. This may be attributed 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

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 demonestrate bathochromic shift in non-hydrogen bonding solvents (NHB) which is attributed to the change in the structures from non-polar state to polymothine 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, β-, α), were successful.Strong deviation was observed in case of alcoholic solvents relative to the non alcoholic ones (HBA and NHB), this deviation is actributed to strong interaction between these alcoholic solvents and the investigated compounds I-IV (cf. Table 3).

In conclusion, the results demonestrate the existance 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.

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, $HL + H \rightleftharpoons H_2L$. 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 (λ_{max}) 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].

$$\frac{[A]\,[D]}{d} = \frac{[D]}{\varepsilon_c} + \frac{1}{K\,\varepsilon_c}$$

Where [D] is donor quantities ranging from 0.0% to 6%, [A] is acceptor quantity, d is absorbance at λ_{max}, ε_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. $M+H^+ \rightleftharpoons MH^+$ 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 I is more basic than II.

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°). It gives the molecular ion peaks at m/z=337 and base peaks at m/z=195 at all investigated temperatures. (Table 4) shows that with increasing, the temperature from 95 to 200 C° the half life time of the ions decrease.

Also 120 C° 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 cereus, 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.

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دراسات طيفية لبعض مشتقات اوكزازولين -٥-١ون ذات مجموعات معطيه ومكتسبه للالكترون

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الملخص العربي

حضرت بعض مشتقات الاوكزازولين -٥-١ون وتم دراسة اطياف الامتصاص الالكترونية في المذيبات العضوية ذات القطبية المختلفة وذلك في منطقة الطيف المرئي والاشعة فوق البنفسجية. كذلك تم دراسة طيف الامتصاص لبعض المشتقات المحتوي على $-N(CH_3)_2$ في محاليل مائية ذات ارقام هيدروجينية مختلفة وقد تم حساب ثابت الاتزان. كذلك تم حساب ثابت الاتزان عند دراسة طيف الامتصاص لبعض هذه المشتقات في مخلوط من مذيبين احدهما له خواص حمضية والاخر له خواص قاعدية. بالاضافة الى ذلك تم دراسة طيف الكتله عند درجات الحرارة المختلفه وايضا التاثير البيولوجي لهذه المركبات على بعض انواع من البكتريا والفطريات.

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Vol 17 (1992).

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

Solvent	ET K.cal mol^{-1}	Z	α	β	Dielectric constant at 20 c°	I	II	I	II	I	II	I	II
						λ_{max} (n m)		Transition energy (ev)		ε_{max} $L.mol^{-1}.cm^{-1}$		$\Delta\bar{\nu}_{\frac{1}{2}}$ cm^{-1}	
DOD ← A :													
MeOH	55.5	83.6	0.93		32.6	527	498	2.352	2.489	25914	45436	4182	3698
EtOH	51.9	79.6	0.950		24.3	532	498	2.330	2.489	31961	43831	4033	3670
iso-PrOH	48.9	76.3	0.697		18.3	535	503	2.317	2.465	25611	40622	4003	3751
DDA :													
DMSO	45.0	71.3		0.752	48.9	545	512	2.275	2.421	26479	42040	3755	3724
DMF	43.5	68.5		0.710	36.7	539	507	2.300	2.445	27344	36721	3970	3204
Acetone	42.2	65.7		0.489	20.7	526	495	2.357	2.505	31372	44066	4120	3734
Ethyl acetate	38.1	59.4		0.481	6.0	519	490	2.389	2.530	36805	34704	4387	3631
Dioxan	36.0	--		0.363	2.2	517	489	2.398	2.540	37208	36960	4040	3577
NDD													
CH_2Cl_2	41.1	64.2			8.9	542	507	2.287	2.445	26217	32317	3567	3538
Benzene	34.5	--			2.3	530	495	2.339	2.505	28125	39568	3611	3426
Toluene	33.9	--			2.4	528	494	2.348	2.510	30760	40621	3900	3525
CCl_4	32.5				2.2	520	481 502 sh	2.384	2.577	35040	38014	3762	3042
Cyclohexane	31.2	--			2.0	500	468* 494	2.480	2.649	32772	39618	3586	2975
n-Hexane	30.9	--			1.9	500	464* 487	2.480	2.672	17098	30311	4041	3532

* Two Maxima.

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

Solvent	E_T K.cal mol^{-1}	Z	α	β	Dielectric constant at 20 c°	III λ_{max} (n m)	IV λ_{max} (n m)	III Transition energy (ev)	IV Transition energy (ev)	III ϵ_{max} $L.mol^{-1}.cm^{-1}$	IV ϵ_{max} $L.mol^{-1}.cm^{-1}$	III $\Delta\bar{\nu}_{1/2}$ cm^{-1}	IV $\Delta\bar{\nu}_{1/2}$ cm^{-1}
HBD - A -													
MeOH	55.5	93.6	0.98		32.6	403	375	3.078	3.306	26000	26909	4418	4612
EtOH	51.9	79.6	0.850		24.3	405	377	3.061	3.289	33100	28183	4321	4868
iso-PrOH	48.9	76.3	0.687		18.3	408	379	3.054	3.271	28028	30232	4201	4880
HBA													
DMSO	45.0	71.1		0.752	48.8	412	385	3.009	3.139	32321	27048	4538	4923
DMF	43.8	68.5		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		0.481	6.0	403	377	3.076	3.269	43750	31857	4387	4855
Dioxan	36.0	--		0.363	2.2	403 393 sh	378 366 sh	3.078	3.280	41200	30296	4206	4609
NHD													
CH_2Cl_2	41.1	64.2			8.9	412 393 sh	383 368 sh	3.009	3.237	37650	19778	4533	3699
Benzene	34.5	--			2.3	410	386 370 sh	3.024	3.212	39750	27075	4359	4499
Toluene	33.9	--			2.4	409	386 368 sh	3.031	3.212	41750	31202	3920	4931
CCl_4	32.5				2.2	409 434 sh	387 370 sh	3.031	3.204	40750	30699	3834	2752
Cyclohexane	31.2	--			2.0	405 427 sh 386 sh	384 367 sh	3.061	3.229	46250	30951	3169	2025
n-Hexane	30.9	--			1.9	401 422 sh	380 363 sh 402 sh	3.092	3.263	46250	30951	3387	3753

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

Compound	Linear equation	Solvent	X	Y	Linear equation	Solvent	X	Y
I	$y=1.919 \times 10^{-3} X + 1.995$	MeOH,EtOH,Iso-PrOH	Z	Ecr (ev)	$y=5.830 \times 10^{-3} X + 2.055$	MeOH,EtOH,Iso-PrOH	ET	Ect(ev)
	$\rho=0.9955$				$\rho=0.9955$			
II	$y=3.173 \times 10^{-3} X + 2.228$				$y=3.517 \times 10^{-3} X + 2.293$			
	$\rho=0.9371$				$\rho=0.9396$			
III	$y=3.039 \times 10^{-3} X + 2.621$				$y=3.360 \times 10^{-3} X + 2.659$			
	$\rho=0.9865$				$\rho=0.9901$			
IV	$y=4.776 \times 10^{-3} X + 2.907$				$y=5.264 \times 10^{-3} X + 3.013$			
	$\rho=0.9974$				$\rho=0.9976$			
I	$y=-1.005 \times 10^{-2} X + 2.999$	DMSO,DMF,Acetone,	Z	Ect (ev)	$y=-1.038 \times 10^{-2} X + 3.027$	DMSO,DMF,Acetone,	ET	Ect(ev)
	$\rho=-0.9053$	Ethyl acetate			$\rho=-0.9537$	Ethyl acetate		
II	$y=-9.934 \times 10^{-3} X + 3.106$				$y=-1.582 \times 10^{-2} X + 3.136$			
	$\rho=-0.9434$				$\rho=-0.9259$			
III	$y=-5.691 \times 10^{-3} X + 3.422$				$y=-9.220 \times 10^{-3} X + 3.436$			
	$\rho=-0.5011$				$\rho=-0.8744$			
IV	$y=-1.000 \times 10^{-2} X + 3.049$				$y=-1.691 \times 10^{-2} X + 3.095$			
	$\rho=-0.7251$				$\rho=-0.9769$			
I	$y=0.135 X + 2.230$	MeOH,EtOH,Iso-PrOH		Ect (ev)	$y=-3.810 \times 10^{-2} X + 3.645$	Benzene,Toluene,	ET	Ect(ev)
	$\rho=0.9819$				$\rho=-0.9749$	CCl4,Cyclohexane,		
II	$y=0.0511 X + 2.413$				$y=-1.785 \times 10^{-2} X + 4.143$	n-Hexane		
	$\rho=0.8871$				$\rho=-0.9903$			
III	$y=0.0715 X + 3.003$				$y=-1.585 \times 10^{-2} X + 3.558$			
	$\rho=0.9687$				$\rho=-0.9736$			
IV	$y=0.115 X + 3.152$				$y=-1.090 \times 10^{-2} X + 3.576$			
	$\rho=0.9996$				$\rho=-0.7281$			

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	43.3	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	Lucillus cereus	Bacillus subtilis	Aspergillus niger	Penicillium cyclopium
II	800	20	26	10	18	20	14
	500	8	12	0	0	8	6
	100	0	0	0	0	0	0
	50	0	0	0	0	0	0
III	800	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

Univ. Coll. Ann. Rev.
Vol 17 (1992).

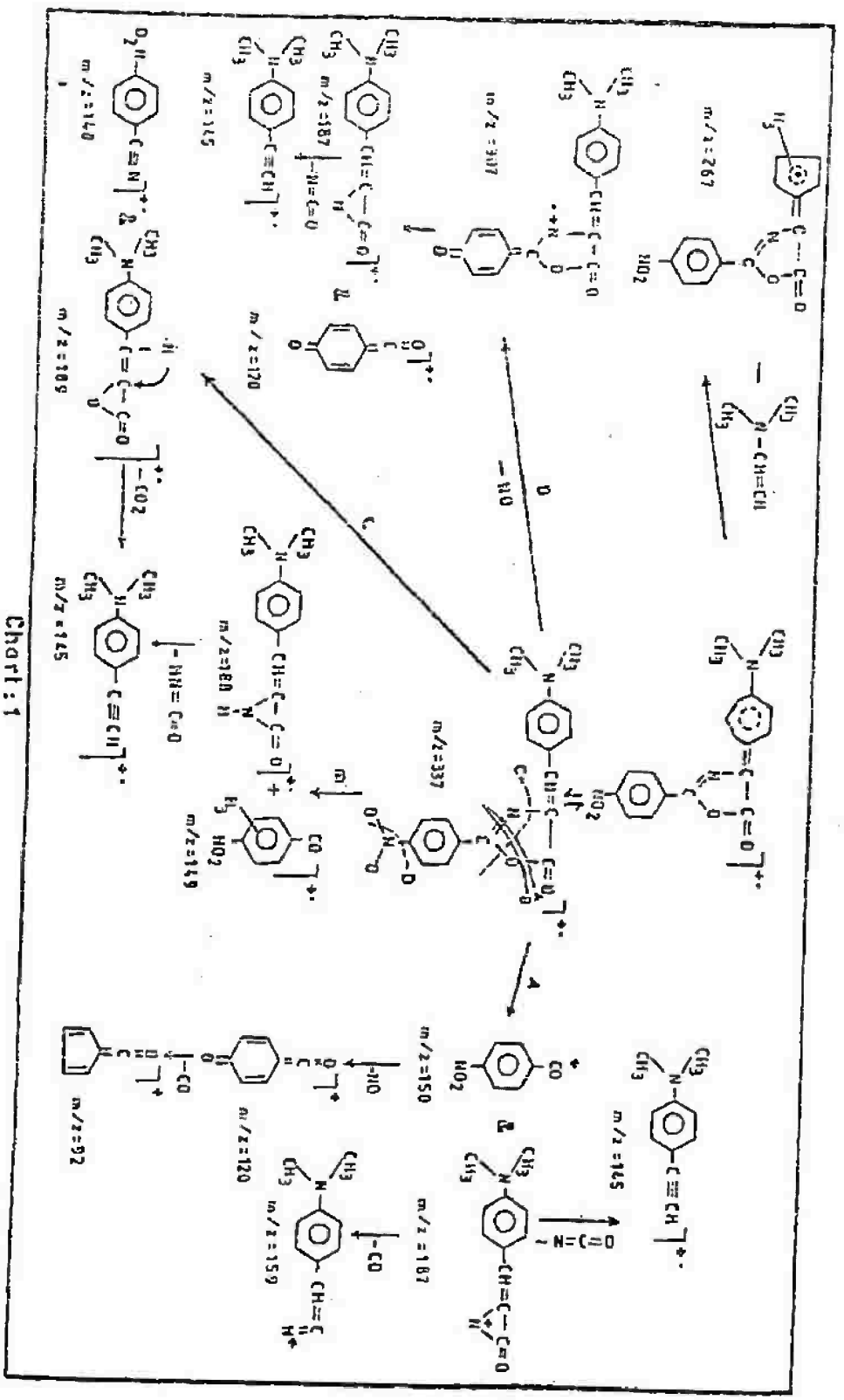

Chart : 1