Spectroscopic Studies on 4-(*p*-Dimethylaminobenzylidene) and 4-(*p*-Dimethylaminophenylimino) Derivatives of 3-Methyl-1-phenyl-2-pyrazolin-5-one

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The electronic absorption spectra of 4-(*p*-dimethylaminoben-zylidene) and 4-(*p*-dimethylaminophenylimino) derivatives of 3--methyl-1-phenyl-2-pyrazolin-5-one were studied in polar and nonpolar solvents. HMO and PPP calculations were done to investigate the first $\pi \rightarrow \pi^*$ transition and the effect of replacing the backbone carbon atom C-13 in 4-*p*-dimethylaminobenzylidene-3--methyl-1-phenyl-2-pyrazolin-5-one by a nitrogen atom. The electron densities of these compounds were calculated by the SCF--method.

INTRODUCTION

Pyrazolone dyes have found wide applications as photosensitizers[1], dye-stuffs[2], analytical[3] and Antitubercular[4] reagents. Little attention has been focused on the electronic absorption spectra of such compounds though the effect of substitution at the phenyl group of 4-arylidene-3-methyl-1-phenyl--2-pyrazolin-5-ones on their spectral behaviour has been studied.[5]

EXPERIMENTAL

4-(*p*-Dimethylaminobenzylidene) and (4-*p*-dimethylaminophenylimino) deriva-tives of 3-methyl-1-phenyl-2-pyrazolin-5-one (compounds I and II respectively) were prepared by refluxing equimolar ratios of 3-methyl-1-phenyl-2-pyrazolin-5-one[6] and *p*-dimethylaminobenzaldehyde or *N,N*-dimethyl-*p*-nitrosoaniline in ethanol con-taining piperidine as catalyst[1]. The separated solid products were recrystallized from ethanol. The purity of the compounds was checked by chemical analysis, Table I.

Spectral grade quality solvents (BDH or E. Merck) were used.

Stock solutions (10^{-3} M) were made by dissolving an accurately weighed amount of the dye in the appropriate volume of solvent. Dilute solutions for spectral measurements were obtained by accurate dilution.

The electronic absorption spectra were recorded at 27 °C on a Shimadzu UV-200 S double beam spectrophotometer, using 1-cm matched silica cell.

RESULTS AND DISCUSSION

The electronic absorption spectra of compounds I and II in polar and nonpolar solvents are given in Figures 1. and 2. The λ_{max} and ε_{max} values of the absorption bands in the solvents used are collected in Tables II and III.

The Elemental Analysis Data and Melting Points of Compounds

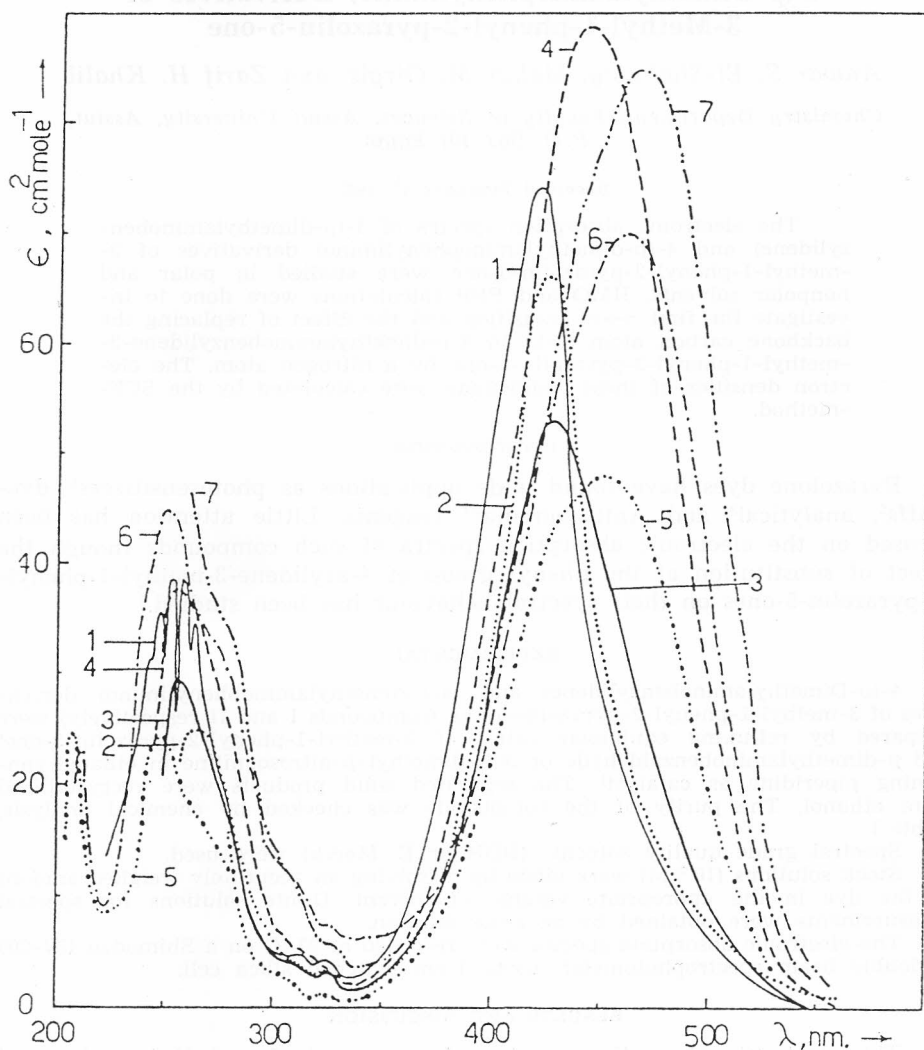| Compound	Formula	m. p. °C	Found (Calc.) %		
			C	H	N
I	$C_{19}H_{19}N_3O$	185	74.64 (74.73)	6.18 (6.27)	13.71 (13.76)
II	$C_{18}H_{18}N_4O$	165	70.49 (70.59)	5.92 (5.88)	18.19 (18.29)

Figure 1. The electronic absorption spectra of compound I in pure organic solvents at 27 °C: 1) C_6H_{12}; 2) CCl_4; 3) dioxane; 4) $CHCl_3$; 5) isopropanol; 6) ethanol and 7) DMSO.
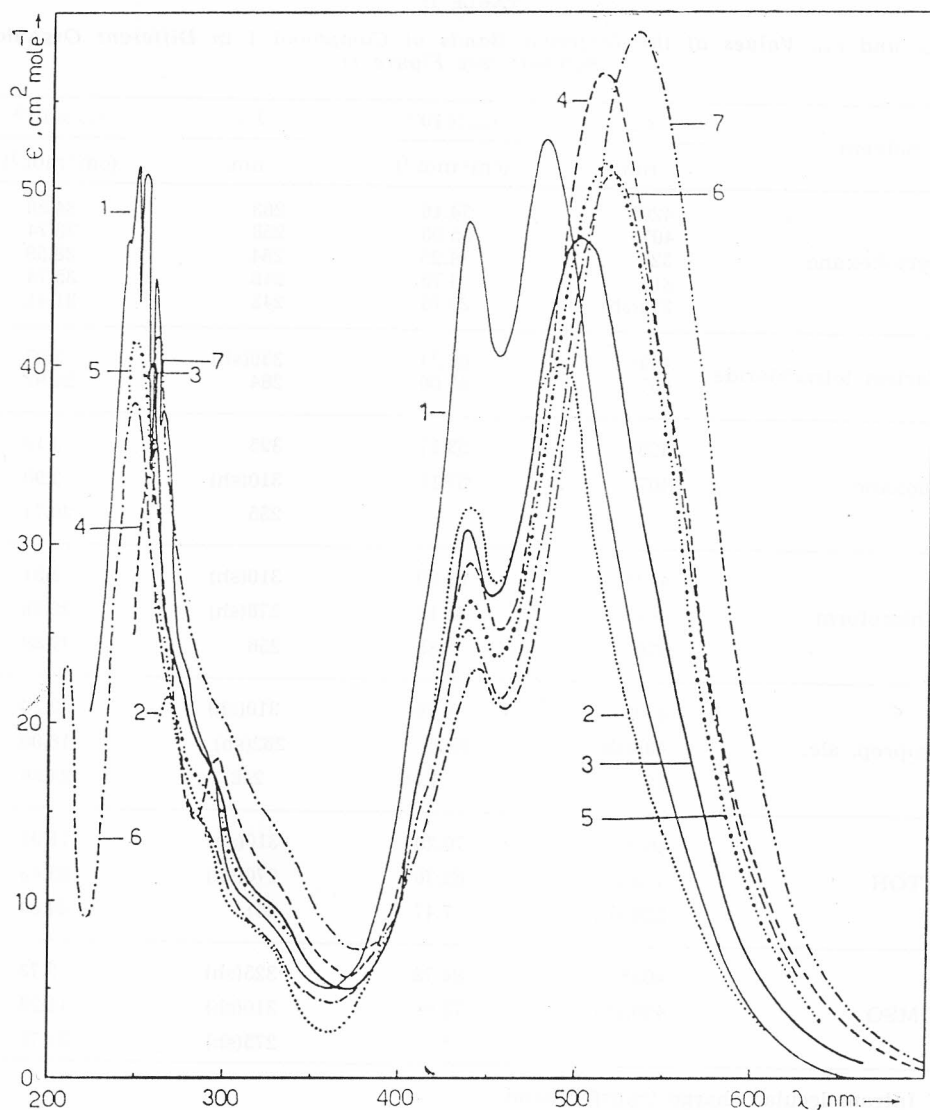
Figure 2. The electronic absorption spectra of compound II in pure organic solvents at 27 °C: 1) C_6H_{12}; 2) CCl_4; 3) dioxane; 4) $CHCl_3$; 5) isopropanol; 6) ethanol and 7) DMSO.

The plots of $\Delta \bar{\nu}$ as a function of $(D-1)/(D+1)^7$ for compounds (I) and (II) are nonlinear, cf. Table IV. Therefore the band shift is governed by other factors in addition to the dielectric constant of the medium. These factors include solute-solvent interactions.

The CT bands of compounds (I) and (II) (420 nm and 481 nm, respectively) are affected by the polarity of the solvent, Tables II and III.

TABLE II

λ_{max} and ε_{max} *Values of the Different Bands of Compound I in Different Organic Solvents (see Figure 1)*

Solvent	λ_{max} nm	$\varepsilon_{max} \times 10^{-3}$ (cm^2 mol^{-1})	λ_{max} nm	$\varepsilon_{max} \times 10^{-3}$ (cm^2 mol^{-1})
Cyclohexane	420*	74.16	263	34.58
	407	55.00	258	38.74
	326	4.25	254	38.58
	313	4.75	248	35.74
	275(sh)	20.75	243	31.41
Carbon tetrachloride	425*	66.24	330(sh)	3.07
	407	45.00	264	24.92
Dioxane	428*	53.17	325	3.19
	407	37.15	310(sh)	3.90
			255	29.74
Chloroform	442*	88.90	310(sh)	5.51
	407	45.12	278(sh)	26.66
	328	2.85	256	37.88
Isoprop. alc.	450*	48.06	310(sh)	2.20
	439(sh)	46.20	262(sh)	18.00
	325	1.15	248	24.39
ETOH	460*	70.20	310(sh)	11.01
	439(sh)	62.30	270(sh)	33.43
	326(sh)	7.47	251	44.84
DMSO	465*	84.78	325(sh)	5.73
	439(sh)	73.02	310(sh)	11.23
			275(sh)	31.75

* Intramolecular charge transfer band.

The observed red shift can be explained by the increase of the hydrogen bond strength between solute and solvent. Intermolecular hydrogen bonding leads to the formation of a solute-solvent molecular complex. The value of the formation constant K_f of the complex with ethanol was determined from the spectral behaviour in mixed solvents (see Figures 3—6) using the relations previously described.[8-10]

The values of K_f, ΔG (free energy change of formation) and n (the number of ETOH molecules which are complexed with the solute molecule) indicate that a 1:1 complex is formed. The value of K_f is dependent on both the solute and the solvent used, cf. Table V.

The HMO and SCF (PPP) calculations were done as described before.[11,12] The HMO calculations give the eigenvalues of HOMO and LUMO for the two compounds (I and II) shown in Table VI.

TABLE III

λ_{max} and ε_{max} Values of the Different Bands of Compound II in Different Organic Solvents (see Figure 2)

Solvent	λ_{max} nm	$\varepsilon_{max} \times 10^{-3}$ (cm² mol⁻¹)	λ_{max} nm	$\varepsilon_{max} \times 10^{-3}$ (cm² mol⁻¹)
Cyclohexane	481*	52.81	264	37.39
	437	48.15	259	45.02
	323(sh)	8.90	253	50.84
	290(sh)	18.33	249	51.35
	277	23.50	244	47.06
Carbon tetrachloride			325(sh)	8.57
	488*	40.25	297(sh)	12.80
	439	32.16	267	22.98
Dioxane			325(sh)	10.05
	500*	47.24	295(sh)	16.90
	439	28.89	258	40.38
Chloroform			325(sh)	11.82
	512*	56.52	297	17.85
	438	30.85	256	33.81
Isoprop. alc.			325(sh)	9.70
	513*	51.49	295(sh)	15.70
	439	26.76	249	41.35
EtOH			325(sh)	8.21
	518*	50.83	297(sh)	12.96
	439	25.12	248	37.86
DMSO			325(sh)	14.75
	532*	58.89	297(sh)	20.50
	445	23.00	261	41.61

* Intramolecular charge transfer band.
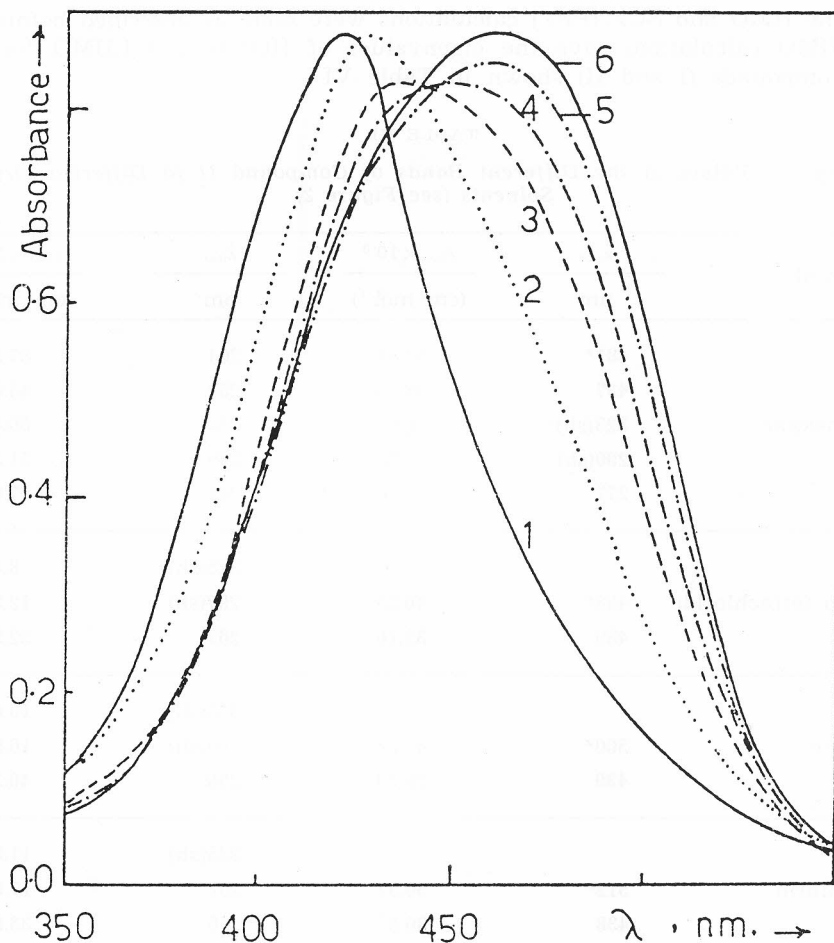
Figure 3. The electronic absorption spectra of 1.25×10^{-5} M of compound I in EtOH—CCl₄ solution mixtures at 27 °C: 1) 0.00; 2) 1.20; 3) 4.63; 4) 8.07; 5) 14.08 and 6) 17.17 M ethanol.

TABLE IV

The Relation Between Spectral Shifts of the CT Bands for Compounds I and II with Respect to Cyclohexane

Solvent	$\bar{\nu}/\text{cm}^{-1}$ (I)	$\bar{\nu}/\text{cm}^{-1}$ (II)	$\Delta\bar{\nu}\times 10^{-2}$ (I)	$\Delta\bar{\nu}\times 10^{-2}$ (II)	$\dfrac{D-1}{D+1}\times 10$
Cyclohexane	23809	20790	0	0	3.33
Carbon tetrachloride	23529	20492	2.80	2.98	3.75
Dioxane	23364	20000	4.45	7.90	3.77
Chloroform	22624	19531	11.85	12.59	6.55
Isoprop. alc.	22222	19493	15.87	12.97	8.96
EtOH	21739	19305	20.70	14.85	9.21
DMSO	21505	18797	23.04	19.93	9.58

D: is the dielectric constant of the solvent.
$\Delta\nu$: is the CT band shift, cm⁻¹.

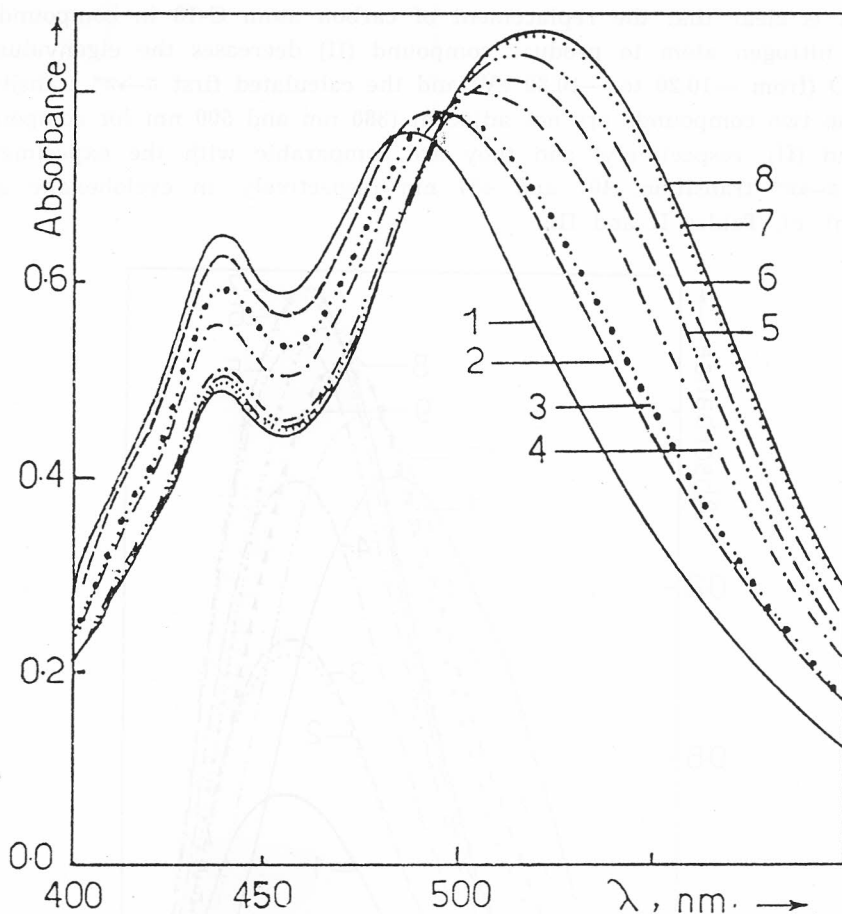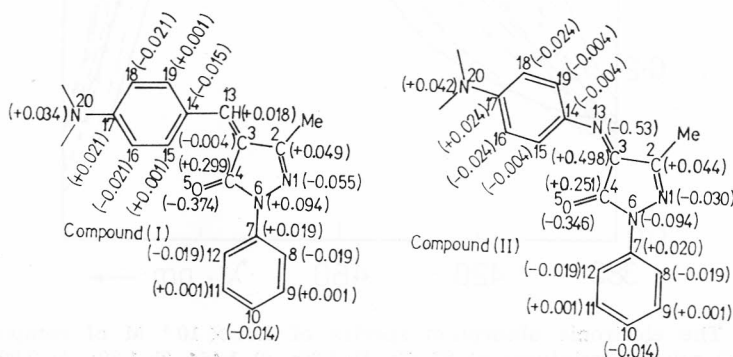Figure 4. The electronic absorption spectra of 1.69×10^{-5} M of compound II in EtOH—CCl$_4$ solution mixtures at 27 °C: 1) 0.00; 2) 0.86; 3) 1.72; 4) 5.15; 5) 8.58; 6) 11.16; 7) 14.59 and 8) 17.17 M ethanol.

Charge densities distribution over compounds (I) and (II).

It is clear that the replacement of carbon atom C-13 in compound (I) by a nitrogen atom to produce compound (II) decreases the eigenvalue of LUMO (from —10.20 to —10.89 eV) and the calculated first $\pi \rightarrow \pi^*$ transitions for the two compounds are not adjacent (380 nm and 500 nm for compounds (I) and (II), respectively) and they are comparable with the experimental first $\pi \rightarrow \pi^*$ transition, 407 and 437 nm respectively, in cyclohexane as a solvent, cf. Tables II and III.
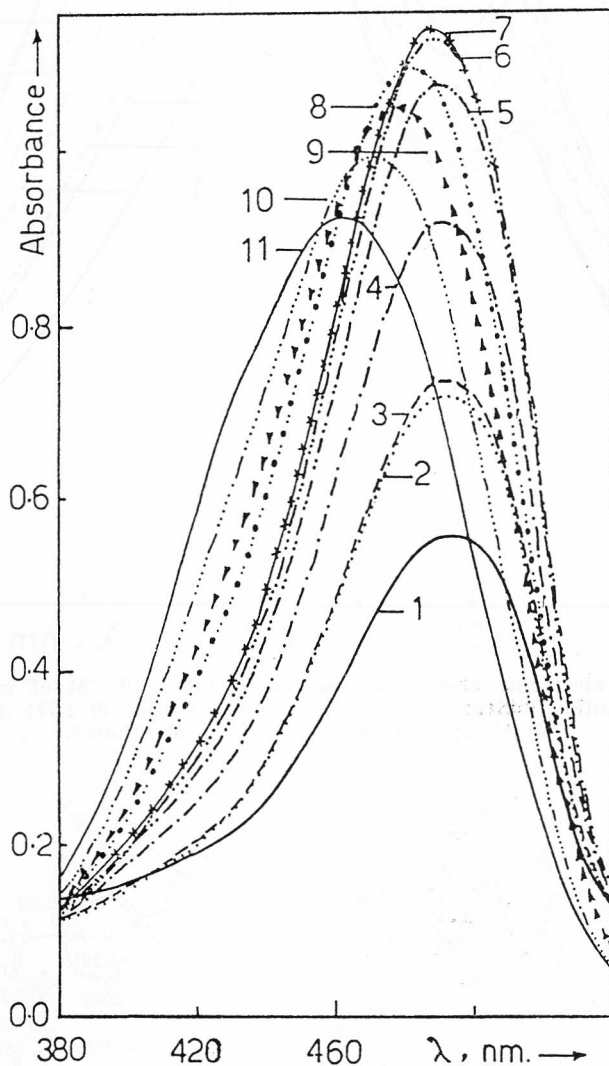

Figure 5. The electronic absorption spectra of 1.31×10^{-5} M of compound I in EtOH—H$_2$O solution mixtures at 27 °C: 1) 1.20; 2) 1.46; 3) 1.80; 4) 2.06; 5) 2.92; 6) 3.78; 7) 4.63; 8) 8.07; 9) 10.64; 10) 14.08 and 11) 17.17 M ethanol.

The SCF-eigenfunctions of HOMO and LUMO for the two compounds are given in Table VII. From the constructions of the SCF-eigenfunctions of HOMO and LUMO it is clear that these eingenfunctions are mainly located over the 4-dimethylaminobenzylidene part of the molecule in compound I and over the 4-dimethylaminophenylimino part in compound II. The local symmetry of HOMO and LUMO for the two compounds is B_2; therefore the first $\pi \to \pi^*$ transition for the two compounds is allowed, and its molar absorbance has a high value ($\varepsilon_I = 55 \times 10^3$ and $\varepsilon_{II} = 48.5 \times 10^3$ mol^{-1} cm^2). Also, it is noticed that the contribution of atom 13 in HOMO is smaller than that in LUMO. This explains that the variation in the HOMO energy is smaller than the variation in the energy of LUMO after the replacement of the carbon atom in position 13 by nitrogen atom in compound I.

The electron densities of compounds (I) and (II) were calculated as described before[11], Table VIII.
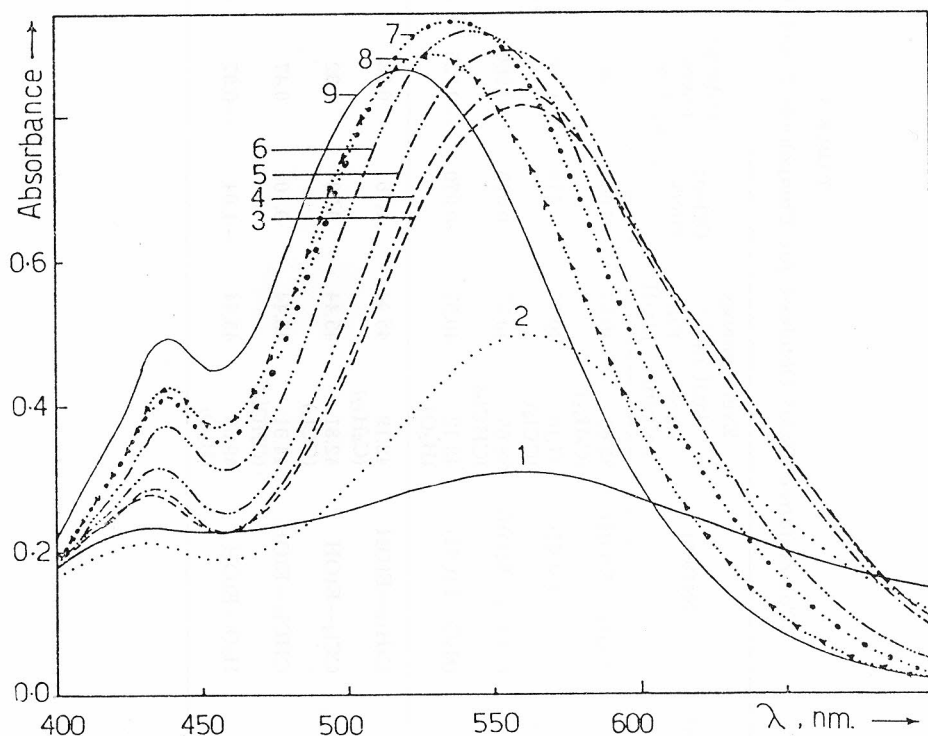

Figure 6. The electronic absorption spectra of 1.69×10^{-5} M of compound II in EtOH—H$_2$O solution mixtures at 27 °C: 1) 1.72; 2) 2.57; 3) 3.43; 4) 4.29; 5) 5.15; 6) 6.01; 7) 11.16; 8) 14.76 and 9) 17.17 M ethanol.

TABLE V

Commutative Data[1] Obtained for Compounds I and II in Mixed Organic Solvents

Compound	System	Excit. energy $kcal \cdot mol^{-1}$		Orient. energy	H-bond energy $kcal \cdot mol^{-1}$	Total energy	n	$\log K_f$	K_f	$-\Delta G$ $kcal \cdot mol^{-1}$
		Pure solvent	Pure EtOH							
I	$(C_6H_{12}$—EtOH)	35.65 (C_6H_{12})	40.57	3.000	0.960	3.960	1	0.350	2.24	0.485
	$(CCl_4$—EtOH)	37.10 (CCl_4)	40.57	1.110	1.590	2.700	1	0.000	1.00	0.000
	$(CHCl_3$—EtOH)	38.65 $(CHCl_3)$	40.57	0.520	0.960	1.380	1	0.295	1.97	0.408
	$(H_2O$—EtOH)	43.12 (H_2O)	40.57	—0.970	—0.725	—1.695	2	0.140	1.38	0.194
II	C_6H_{12}—EtOH	42.19 (C_6H_{12})	45.44	1.76	0.88	2.64	1	0.43	2.69	0.595
	CCl_4—EtOH	42.81 (CCl_4)	45.44	0.70	1.32	2.02	1	0.288	1.94	0.399
	$CHCl_3$—EtOH	44.91 $(CHCl_3)$	45.44	0.10	0.47	0.57	1	0.424	2.65	0.586
	H_2O—EtOH	49.65 (H_2O)	45.44	—1.04	—0.97	—2.01	2	0.600	3.98	0.831

[1] at 27 °C.

TABLE VI

Eigenvalues of HOMO and LUMO for Compounds I and II

Compound	ε_{HOMO}/ev	ε_{LUMO}/ev
I	—13.46	—10.20
II	—13.37	—10.89

TABLE VII

The SCF-eigenfunctions of HOMO and LUMO for the Two Compounds

Atomic orbital	HOMO (I)	HOMO (II)	LUMO (I)	LUMO (II)
Φ_1	0.134	0.081	0.127	0.234
Φ_2	0.108	0.051	—0.111	—0.120
Φ_3	—0.197	—0.170	—0.197	—0.690
Φ_4	0.033	0.011	—0.687	—0.348
Φ_5	0.201	0.088	0.505	0.330
Φ_6	—0.203	—0.053	0.124	0.065
Φ_7	0.210	0.042	0.085	0.014
Φ_8	0.141	0.031	—0.065	—0.020
Φ_9	—0.091	—0.018	—0.035	—0.005
Φ_{10}	—0.218	—0.045	0.092	0.022
Φ_{11}	—0.091	—0.018	—0.035	—0.005
Φ_{12}	0.141	0.031	—0.065	—0.020
Φ_{13}	—0.152	—0.131	0.316	0.383
Φ_{14}	0.434	0.511	0.128	0.089
Φ_{15}	0.210	0.248	—0.106	—0.140
Φ_{16}	—0.256	—0.298	—0.046	—0.023
Φ_{17}	—0.427	—0.490	—0.142	0.152
Φ_{18}	—0.257	0.298	—0.047	—0.023
Φ_{19}	0.209	0.248	—0.105	—0.140
Φ_{20}	0.297	0.355	—0.031	—0.043

From the values of charge densities of the two compounds, *cf.* Table VIII the carbon atom C-3 in the pyrazoline moiety acts as a strong donor in compound II, but it acts as a weak acceptor in compound I. Carbon atom C-13 acts as a weak donor in compound I although the nitrogen atom at position 13 in compound II acts as a strong acceptor.

It is clear that the oxygen atom in compound (I) is more negative than that in compound (II). Therefore, the energy of the intermolecular hydrogen bond in compound (I) is higher than that in compound (II) in different mixed solvents, *cf.* Table V. It is concluded that the oxygen atom in position 5

TABLE VIII

SCF-electron Densities and Charge Densities of Compounds I and II

Atom	Compound I		Compound II	
	Electron densities	Charge densities	Electron densities	Charge densities
1	1.055	—0.055	1.030	—0.030
2	0.951	+0.049	0.956	+0.044
3	1.004	—0.004	0.502	+0.493
4	0.700	+0.299	0.749	+0.251
5	1.374	—0.374	1.346	—0.346
6	1.906	+0.094	1.906	+0.094
7	0.981	+0.019	0.980	+0.020
8	1.019	—0.019	1.019	—0.019
9	0.999	+0.001	0.999	+0.001
10	1.014	—0.014	1.014	—0.014
11	0.999	+0.001	0.999	+0.001
12	1.019	—0.019	1.019	—0.019
14	1.015	—0.015	1.004	—0.004
15	0.999	+0.001	1.004	—0.004
16	1.020	—0.021	1.024	—0.024
17	0.978	+0.021	0.976	+0.024
18	1.020	—0.021	1.024	—0.024
19	0.999	+0.0014	1.004	—0.004
20	1.966	+0.034	1.958	+0.042

is the negative pole of the intermolecular hydrogen bonding between the solute and the solvent.

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SAŽETAK

Spektroskopski studij 4-(p-dimetilaminobenzil)- i 4-(p-dimetilaminofenilimino)--derivata 3-metil-1-fenil-2-pirazolin-5-ona

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Istražen je utjecaj polarnosti medija na elektronske apsorpcijske spektre 4-(p-dimetilaminobenziliden)-3-metil-1-fenil-2-pirazolin-5-ona (*I*). Izmjereni spektri korelirani su sa spektrima 4-(p-dimetilaminobenziliden)-3-metil-1-fenil-2-pirazolin--5-ona (*II*). Razlike između spektara *I* i *II* objašnjene su na bazi rezultata HMO i PPP računa.