UV/Vis, IR and ^{1}H NMR spectroscopic studies of bisazo-dianil compounds based on pyrimidenyl azo hydroxybenzaldehyde derivatives and primary aliphatic diamines

Raafat M.Issa, Samy A.EI-Daly, Nadia A.El-Wakiel*, Ramadan A.Mansour
Chemistry Department, Faculty of Science, Tanta University, Tanta, (EGYPT)
E-mail : drnadia64@hotmail.com, drnadia6@yahoo.com
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ABSTRACT

A series of newly prepared bisazo-dianil compounds based on pyrimidenyl azo hydroxybenzaldehyde derivatives and primary aliphatic diamines were synthesized. Their electronic absorption spectra were recorded in organic solvents of varying polarity and in buffer solutions of different pH. The absorption bands were assigned to the corresponding electronic transitions characteristic of the molecules, the effect of solvent polarity and pH of the medium on band maxima were discussed. The change of absorption spectra with pH was utilized to calculate the acid dissociation constants of the compounds. Also the important bands of IR and signals of ^{1}H NMR spectra of the compounds were studied, as well as their fluorescence spectra are considered. Also the pathological studies of this compounds on Pitrysporum ovale and Pitrysporum orbiculare isolated from different cases of tinea versicolor were studied.

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INTRODUCTION

Many azo compounds have been used as chromogenic reagents for the spectrophotometric determination of small amounts of metal ions. The application of these azo compounds in spectral analysis depends essentially on their UV/Vis characteristics. Many articles have been devoted to study the spectral behavior of azo compounds[1-3], also a considerable number of papers were published on the spectra of Schiff bases (azomethines or anils)[6]. In addition it was reported that azomethines can function as dyestuffs[7,8].
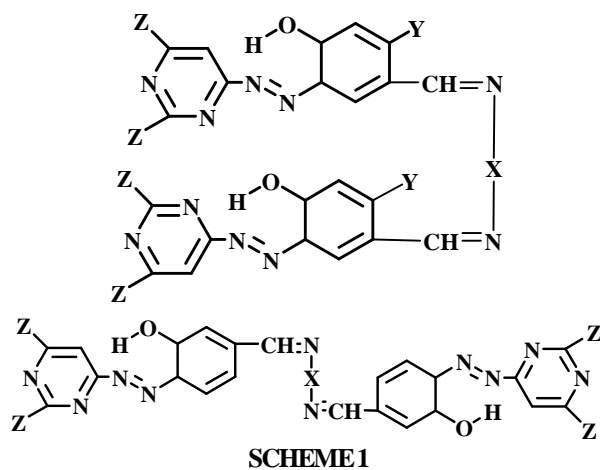
Although the studies of azo-or azomethine compounds drew the attention of many workers, yet few studies delt with the spectral behaviour of azo-azomethines[9,10], dianis[11,12] or bisazodianils[13].A new azodye called (S D-l dye), has been recently synthesized and usefully tested for the alignment of nematic liquid crystals[14]. Recently, some azodyes were used for preparing dye-doped polymers[15].

In the present article, we consider the spectral properties of a new group of bisazodianils based on pyrimidenylazo hydroxybenzaldehydes and aliphatic diamines. These compounds were found to form polynuclear complexes with transitions metal ions[16]. It is aimed to throw light on the UV/Vis, IR and ^{1}H NMR spectra of these compounds. Also their fluorescence spectra are considered.

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EXPERIMENTAL

All compounds used in the present study were of highest purity available from Aldrich, Sigma or BDH. The solvents were spectroscopic grade and used as supplied, the azodyes based on 4-aminopyrimidene derivatives and 2,4-dihydroxy. 4-hydroxy or 3-hydroxybenzaldehydes were prepared according to the procedure given previously[17]. The bisazodianil compounds (I-XII) were prepared by condensation of the azo compounds with the aliphatic diamines in the usual manner for preparing Schiff bases[18]. The purity of the compounds prepared was supported from the data of elemental analysis and TLC experiments. Minimal inhibitory concentrations(MIC_s) of the synthetic compounds against *P.ovale* and *P.orbiculare* were determined by linear growth method (Mubarak, 2003). The used media was Sabaroud's dextrose agar. Each culture medium was enriched with different concentrations(100, 75, 50, 25, 1ppm) of these compounds prepared from stock solution. Three Petri dishes were used as replicates for each concentration and three were left without any treatment as control. Each treatment was inoculated centrally with a fungal disk (3 days old). Linear growth was measured daily in cm.

The bisazodianils included in the present study have the general structural formulas given in SCHEME 1.
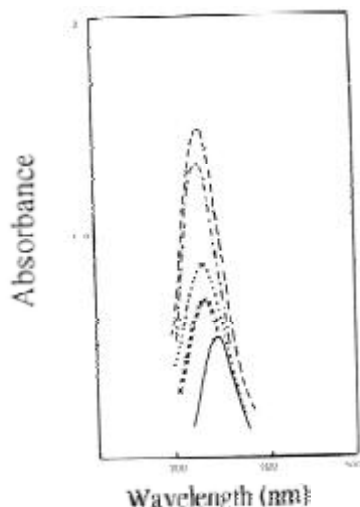
The buffer solutions used for pH control were the components of the Britton and Robinson[9] universal series containing 20 % by volume ethanol. The spectral measurements were carried out at room temperature as given before[1,10]. Steady state fluorescence was measured using Shimadzu RF-510 spectrofluorophotometer using right-angle arrangement. Fluorescence quantum yields (Φ_f) were measured relative to quinine sulfate[20]. Low sample concentration (having ≤0.1 absorbance units at the excitation wavelength) were used to avoid reabsorption.

SCHEME 1

Compounds	x	Y	z
I	$(CH_2)_3$	OH	OH
II	$(CH_2)_6$	OH	OH
III	$(CH_2)_3$	H	CH_3
IV	$(CH_2)_6$	H	CH_3
V	$(CH_2)_3$	H	OH
VI	$(CH_2)_6$	H	OH
VII	$(CH_2)_3$	OH	CH_3
VIII	$(CH_2)_6$	OH	CH_3

Compounds	x	z
IX	$(CH_2)_3$	OH
X	$(CH_2)_6$	OH
XI	$(CH_2)_3$	CH_3
XII	$(CH_2)_6$	CH_3

RESULTS AND DISCUSSION

Electronic absorption spectra in organic solvents

The UV/Vis absorption spectra of compounds I-XII in ethanol exhibit mainly four bands, TABLE 1. The bands (A) and (B) with λ_{max} with 205-300nm range are due to the π-π* transitions within the aromatic rings. Band C seems to be a composite band involving the π-π*, transitions within the C = N and N = N[10] bonds

TABLE 1: Data from electronic absorption spectra in ethanol

I	II	II	IV	V	VI	VII	VIII	IX	X	XI	XII	Assignment
250	230	230	220	240	240	220	242	220	210	206	248	π-π*(Ar)
272	288	244	278	260	288	280	300	278	256	250	288	π-π*(Ar)
336	368	364	368	360	356	310	352	316	344	314	316	π-π*(N=N,C=N)
436	412	476	468	552	428	400	412	400	390	390	400	CT
2.848	3.514	2.915	2.633	2.249	3.901	3.104	3.104	3.104	3.114	3.114	3.104	E_{CT}(ev)
7.372	7.501	7.424	7.220	6.906	7.413	7.567	7.497	7.567	7.575	7.575	7.567	I_p(1)
6.860	6.982	6.897	6.673	6.394	6.972	7.059	6.982	7.059	7.063	7.063	7.059	I_p(2)
7.11	7.228	7.160	7.977	7.694	7.151	7.293	7.230	7.293	7.300	7.300	7.293	I_p(3)
7.108	7.236	7.160	7.957	6.665	7.179	7.309	7.236	7.306	7.313	7.314	7.306	Mean I_p SD

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Figure 1: Electronic absorption spectra of (XI) in (___) DMF,(xxx) Propanol,(…) EtOH,(-.-.-.) Eg and (—) MeOH.

as well as a transition of the chelate rings formed through intramolecular hydrogen bonding between the phonalic OH- groups and N=N or C=N in o-position[21]. Band D is assigned to an intramolecular charge transfer absorption involving the whole molecule as observed for other bisazo dianils[13].

The UV/Vis spectra of l-XII were measured in seven organic solvents of different polarity namely methanol, ethanol, isopropanol, butanol, DMF, acetone, benzene and trichloromethane. The spectra revealed that the two π-π* bands (A, B) are slightly influenced by changing solvent polarity. Bands and D exhibit obvious changes in their position with solvent polarity. The shift of band C indicates that the strength of intramolecular hydrogen bonding is influenced by solvent polarity[22].

The CT band displays a red shift with increased solvent polarity (Figure 1) showing increased solvent stabilization of the excited state in the more polar solvents. The application of the Gati[23] and Szalay or Suppan[24] dielectric relation to the data of the CT band does not lead to linear relationships, this reveals that the dielectric constant of the solvent is not the main factor governing the CT band shift. The plots of E_{CT} as a function of the different molecular microscopic solvent parameters Z[25] E_T[26] α(acidity), β(basicity) and π (dipolarity)[27] show nonlinear relationships donating that these solvent parameters are not the main factors causing the CT band shift. The change in the CT band position is actually the resultant of the different factors governed by the various solvent parameters. These factors

can be additive, counter acting or may even cancel out each other. The use of the Krygowiski and Fawest[28] relationship :

$$Q=Q_o+\alpha\, E_T+\beta D/V$$

In which α and β are the solvent acidity and basicity paratmers, respectively and putting it in the form

$$E_{CT}=E_o+X_oD+X_1Z+X_2\alpha+X_3\beta+X_4\pi$$

gave very low values for the correlation coefficient (r) the value of (r) increased on decreasing the number of solvent parameters considered in the calculation, but its value was still unsatisfactory. On using the linear regression calculation for the various E_{CT} solvent parameters plots, it was found that the values of (r) increased with regression of the points falling far from linearity. Satisfactory linearity (r = 0.868-0.9667) were obtained for ethanol, isoporpanol, DMF, methanol solvents only with Z solvent parameters. This behaviour donates that each solvent parameter will have its effective contribution to CT band shift in certain solvents which also depends on the nature of the solute under study.

The ionization potentials (Ip) of the bisazodianils under study were also determined from the electronic absorption spectra using the relation;

$$Ip=a+bE_{CT}$$

In which E_{CT} is the energy of the CT transition, a and b are constants having the values(4.39 and 0.857) [29], (5.158 and 7780)[30] (5011 and 0.701)[31] in eV. The values thus determined are collected in TABLE 1.

The values of E_{CT} in eV were calculated from the relation

$$E_{CT}=1241/\lambda_{max}\ (nm)$$

Electronic absorption spectra in buffer solutions

The spectra of l-XII were recorded in buffer solutions of pH 2-12, as a matter of fact bands (A) and (B) displayed small changes with rise of pH of the medium. Accordingly the study was confined to bands (C) and (D). The bands (C) and (D) showed only slight increase in their extinctions and small shift of λ_{max} to red in media of pH≤6 at higher pH obvious changes were recorded. For band (D) the extinction increases with rise of pH and its λ_{max} shifts to longer wavelength slightly. The absorbance-pH curves are typical dissociation curves. Band (C) displays some interesting changes with pH, the extinction of the band decreases with rise of pH in the meanwhile a new band is developed at longer wave-

length. The change in spectra is connected with the ionization of the OH groups whereby the H-bonds are destructed and the resulting phenolate ion will contribute to a new intramolecular charge transfer interaction leading to the new band at longer wavelength. For most compounds, as the longer wavelength band is developed it overla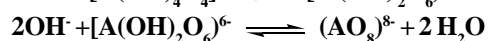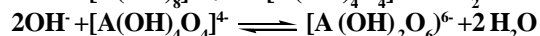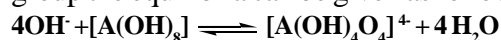ps with band (D) and thereby masking it. Obvious isobestic points were observed for compounds XI and XII containing one type of OH- groups denoting the existence of the acid-base equilibrium of the type

$$A(OH)_2 \ \rightleftharpoons \ A^{-2} + 20H^-$$
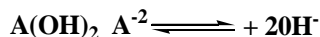
for the other compounds either two isosbestic points are observed for pH ranges 6-8 and 9-12 or deviation from the isosbestic point occurs in solutions of pH higher than 9 as shown in figure 2. This can be ascribed to the existence of more than one equilibrium which are somewhat different from each other e.g. (for compounds III, IV and VII-X)

$$[A(OH)_4] + 20H^- \ \rightleftharpoons \ [A(OH)_2O_2]^{2-} + 2H_2O$$
$$[A(OH)_2O_2]^{2-} + 20H^- \ \rightleftharpoons \ (AO_4)^{4-} + 2H_2O$$
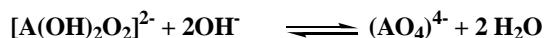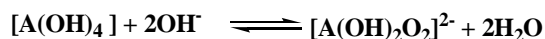
In this case, the first equilibrium in most probably due to the ionization of the OH- groups bonded to the azo nitrogen atoms while the second is due to the OH- groups bonded to the azomethines nitrogen in analogy to the case of simple azo-azomethin dyes[10]. For compounds I and II containing three different types of OH- group the equilibria can be given as follows.

$$4OH^- + [A(OH)_8] \ \rightleftharpoons \ [A(OH)_4O_4]^{4+} + 4H_2O$$
$$2OH^- + [A(OH)_4O_4]^{4+} \ \rightleftharpoons \ [A(OH)_2O_6]^{6-} + 2H_2O$$
$$2OH^- + [A(OH)_2O_6]^{6-} \ \rightleftharpoons \ (AO_8)^{8-} + 2H_2O$$

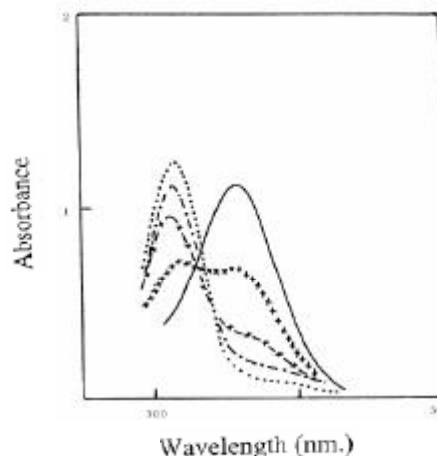The first equilibrium represents the dissociation of the OH groups on the pyrimidinium nucleus. For com-

Figure 2: Electronic absorption spectra of XII in different buffer solutions, (___) pH=11.7, (xxx) pH=9.3,(-x-x-) pH=8.4,(-.-.-) pH=6.7,(…) pH=4.

pounds V and VI, only the first two equilibria can occur. The absorbance-pH curves at $\lambda_{(max)}$ of CT bands are typical dissociation or association curves and also for wavelengths at longer or shorter values near $\lambda_{(max)}$ of the CT band. The variation of absorbance with pH for both bands (C) and (D) was made use of in the determination of the acid dissociation constants of the various OH-groups using the half height, limiting absorbance and modified limiting absorbance methods[32,33]. The results are collected in TABLE 2. The bisazodianils IX -XII show an obvious change in color on going from acidic to neutral than alkaline solutions. This behaviour denotes the probable utility of these compounds as acid-base indicators[34]. Accordingly the halochromic character of these compounds was studied. The halochromism (h) of an acid-base indicator is given by the relation[35].

$$h = \Delta\lambda /\Delta\lambda \ pH$$

TABLE 2: Data obtained from the spectra in buffer solutions

Comp.	Method 1			Method 2			Method 3			Mean values		
	pK$_{a1}$	pk$_{a2}$	pK$_{a3}$	pK$_{a1}$	pK$_{a2}$	pK$_{a3}$	pKa1	pK$_{a2}$	pK$_{a3}$	pKa1	pK$_{a2}$	pK$_{a3}$
I	7.2	9.0	-	6.4	8.6	-	7.8	8.8	-	7.3	8.8	-
II	6.6	9.8	-	6.2	9.6	-	6.6	9.6	-	6.5	9.7	-
III	-	8.0	-	-	7.5	-	-	7.8	-	-	7.8	-
IV	-	8.0	-	-	7.9	-	-	7.9	-	-	7.6	-
V	7.8	8.4	-	7.3	8.0	-	7.8	8.5	-	7.6	8.3	-
VI	6.4	8.2	-	7.0	8.0	-	-	9.2	-	6.7	8.4	-
VII	-	7.6	8.4	-	7.3	8.2	-	7.4	8.2	-	7.4	8.30
VIII	-	9.1	10.0	-	8.8	10.3	-	9.0	9.6	-	8.9	10.0
IX	8.6	8.8	-	8.5	9.0	-	8.6	8.8	-	7.6	8.9	-
X	7.6	8.8	-	7.6	9.3	-	7.6	8.6	-	7.6	8.9	-
XI	-	8.6	-	-	8.3	-	-	8.4	-	-	8.4	-
XII	-	7.0	-	-	8.3	-	-	8.6	-	-	7.9	-

Method 1 half height method, Method 2 limiting absorbance method, Method 3 modified limiting absorbance method

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TABLE 3 : Some diagnostic bands in the IR spectra of the bisazo-dianils under study

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Assignment
3550	3500(sh)	-	-	3500(sh)	3500(sh)	-	-	3560(sh)	3500(sh)	-	-	ν_{OH} bonded
3231	3271	3203	323230	3205	3216	3307	3204	3227	3217	3269	3149	ν_{CH} ar.Asym.
2913	2934	2930	2944	2954	2957	2939	3000	2939	2935	2936	2927	ν_{CH_3} ar asym.
1667	1660	1674	1674	1654	1652	1666	1657	1658	1669	1678	1630	ν_{CH_3} asym
1603	1629	1608	-	-	-	1610	1620					ν_{CH_3} sym
1555	1533	1544	1544	1544	1535	1542	1574	15031394	1527	1504	1535	C=N (H- bonded)
1444	1450	1445	1397	1394	1455	1394	1480	1394	1458	1452	1445	δ_{OH}
1229	1231	1248	1259	1314	1300	1270	1265	1337	1348	1277	1247	ν_{C-N}
1170	1162	1159	1165	1155	1165	1165	1171	1155	1157	1151	1121	ν_{C-OH}
829	849	834	866	849	811	868	845	829	860	830	847	γ_{OH}
855	966	866	889	883	855	923	932	934	923	923	933	γ_{CH} isolated H
833	811	823	777	789	822	856	855	866	866	877	822	$\gamma_{CH\,2}$ adj H
-	-	722	711	705	711	-	-	755	677	788	763	$\gamma_{CH\,3}$ adj H

On plotting the λ(max) as function of pH, a linear correlation is obtained which proceeds according to equation:

$$\lambda = h\,pH + r$$

where 'r ' is a constant corresponds to the wavelength at unit hydrogen ion activity (pH = 0.0), if the change of the colour covers this range of pH and h is a quantity that measures the halochromism.

The variation of λ(max) of band (C) with pH is a typical S- shaped curve indicating the existence of an acid base equilibrium between the nonionsed (acidic) and ionsed (basic) forms of the compounds. The values of h in nm amounted to 57.4 (IX), 47.7 (X), 56.2 (XI) and 49.2 (XII).

IR spectra

The assignments of the important bands in the IR spectra of the bisazodianils under study are collected in TABLE 3.

The IR spectra of compounds (I-XII) show a broad band within the 3400-3100 cm^{-1} range which is assigned to ν_{OH} of the OH groups involved in intramolecular hydrogen bonding with N=N or C=N groups in o-position to it. The free OH- groups in I,II, V, VI, IX, and X display the ν_{OH} band at 3650-3550cm^{-1} mostly appearing as a shoulder. The ν_{cH} of N=CH group lies at 3000-2890cm^{-1} as a weak but sharp band. The aromatic C-H bonds exhibit $\nu_{CH(asym.)}$ at 3195- 3150cm^{-1} and $\nu_{CH(sym.)}$ at 3080-3050cm^{-1} while the CH$_3$ groups of III, IV, VII, VII, VIII, XI, and XII lead to weak bands at 2858-2841cm^{-1} $\nu_{cH\,(asym.)}$ and 2830-2763cm^{-1} $\nu_{cH(sym.)}$. The spectra of I-XII contain medium to strong bands at 1678-1611cm^{-1} due to the C=N stretching mode. The bands at 1605-1530cm^{-1} can be assigned to the C=C of the aromatic rings, the medium intensity band at 1585-1530cm^{-1} corresponds to N=N asym and the band at 1480-1400cm^{-1} is due to the $\nu_{N=N(sym.)}$ stretching mode. The strong band at 1350-1230cm^{-1} is attributed to δ_{OH} while the band at 1270-1205cm^{-1} corresponds to ν_{C-OH} vibration. The in-plane deformation vibration of aliphatic and C-H bonds give a group of sharp bands with the 1400- 1100cm^{-1} Compounds having the CH$_3$ group display the δ_{CH3} characteristic band at 1350-1330cm^{-1}; the out of plane deformation of aromatic CH groups lead to the bands at 955-880cm^{-1} (one isolated hydrogen), 830-780cm^{-1} (two adjacent hydrogen) and 720-670cm^{-1} (three adjacent hydrogen). Despite the fact that the positions of all bands are influenced by the changed molecular structure, yet it is not easy to give general relations in this correction.

¹H NMR spectra

The ¹H NMR spectra of the compounds(I-XII) in

TABLE 4 : Data of ¹H NMR spectra

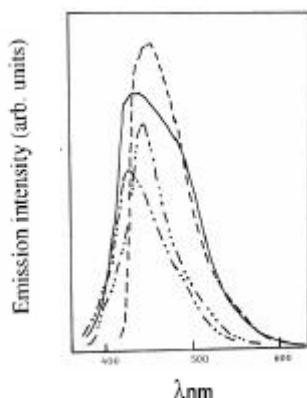| I	II	III	IV	V	VI	XI	XII	Assignment
-	-	1.84	1.45	-	-	-	1.45	CH$_3$(3H)
2.0	3.5	3.5	3.6	3.8	3.6	3.5	3.5	CH$_2$-N(4H)
3.7	3.6	3.8	3.85	3.95	3.75	3.9	3.65	CH$_2$(2 or 8H)
6.6-7.7	6.6-7.8	6.6-8	6.8-8	6.5-8.2	6.7-8.15	7.2-7.9	7.2-7.8	CH Aryl
8.0	8.0	-	-	8.5	8.4	8.5	-	OH(frec) (4H)
8.6	8.57	8.57	8.6	8.69	8.65	8.6	8.66	CH=N(2H)
10.36	10.36	10.3	10.3	10.3	10.3	10.4	10.5	OH(H-bonded)(2H)

Figure 3 : Emission spectra of 1×10⁻⁵ M solutions of IX (-…-), X, (-..-) XI (-), XII (—), in ethanol $\lambda_{ex} = 366nm$

TABLE 5 : Fluorescence maxima and Fluorescence quantum yield of bisazo-dianils compounds in ethanol(λ_{em} = 366nm)

Compound	λ_{em} (max)	φf
I	450	0.004
II	455	0.006
III	495	0.004
IV	495	0.004
V	395	0.004
VI	420	0.0045
VII	415,480	0.003
VIII	425	0.008
IX	390	0.007
X	430	0.006
XI	430	0.008
XII	420	0.01

d⁶ DMSO as solvent display signals corresponding to the various H-atoms. The 'H NMR spectra of all compounds exhibit a signal at 10.5-10.3ppm due to the hydrogen bonded OH-groups. The free OH groups of compounds I, II, VI, IX, and X lead to the signal at 8.5-8.0 ppm (I= 4). The hydrogen of the azomethine group (-CH=N) leads to the signal at 8.7-8.55ppm (I=2); the multisignals of the aromatic H-atoms appear as a complex structure at 8.3-6.5ppm. The aliphatic CH₂- groups show two signals at 3.9-3.6 and 3.8-3.5 ppm, the CH₃ groups of III, IV and XII display a signal at 1.85-1.45ppm(TABLE 4).

The fluorescence spectra

The emission spectra of compounds I-XII were studied in ethanol (Figure 3). The spectra show that there is a good mirror image relationship between absorption and fluorescence spectra. These facts together with the high molar absorptivities are consistent with a strongly allowed transition between the electronic ground and excited states. The fluorescence quantum

TABLE 6: Minimum inhibitory concentrations of the tested compounds against *P.ovale* and *P.orbicularae*

Tested compounds	Conc ppm	P.ovale	Conc ppm	P.orbicularae
		Fungi		
		Inhibition % (I)		
L1	50	14.44	50	11.12
	125	31.73	125	38.27
	250	53.95	250	52.49
	500	79.51	500	86.02
	1000	92.43	1000	100
	2000	100	2000	100
L3	50	18.15	50	31.98
	125	48.89	125	58.15
	250	72.53	250	76.05
	500	100	500	100
	1000	100	1000	100
	2000	100	2000	100
L4	50	12.32	50	19.63
	125	32.72	125	28.77
	250	86.05	250	42.47
	500	97.16	500	62.22
	1000	100	1000	80.62
	2000	100	2000	100
L5	50	32.22	50	42.76
	125	53.46	125	75.44
	250	100	250	100
	500	100	500	100
	1000	100	1000	100
	2000	100	2000	100
L6	50	9.75	50	43.83
	125	21.23	125	52.84
	250	43.35	250	70.37
	500	65.31	500	100
	1000	92.22	1000	100
	2000	100	2000	100
L7	50	15.06	50	23.57
	125	40.86	125	47.98
	250	66.17	250	67.95
	500	84.44	500	100
	1000	97.78	1000	100
	2000	100	2000	100
L8	50	0.00	50	15.30
	125	2.72	125	38.47
	250	10.37	250	64.48
	500	32.96	500	100
	1000	65.29	1000	100
	2000	100	2000	100
L10	50	11.23	50	63.754
	125	33.33	125	89.96
	250	56.17	250	100
	500	78.15	500	100
	1000	86.91	1000	100
	2000	100	2000	100
L11	50	84.53	50	33.49
	125	60.86	125	75.96
	250	100	250	100
	500	100	500	100
	1000	100	1000	100
	2000	100	2000	100
L12	50	0.00	50	53
	125	11.11	125	28
	250	27.78	250	76.21
	500	60.26	500	100
	1000	87.28	1000	100
	2000	100	2000	100

yield (Φ_f) of the compounds was calculated and listed

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in TABLE 5. From these results, one can state that compounds VII and XI give the best fluorescence spectra and satisfactory values for the fluorescence quantum yield. The low values of the fluorescence quantum yields can be explained on the basis of the high flexibility of the molecules. Also the presence of the two azo groups and the hydroxyl groups in the bisazodianil molecule which increases the radiationless processes hence decreases the radiative process.

The antimicrobial activity

The antimicrobial activity of this compounds on Pitrysporum ovale and Pitrysporum orbiculare isolated from different cases of tinea versicolor were studied It was found that the diameter of inhibition zone varied according to both the active group of the synthetic compound and the tested microorganism. The synthetic compounds number L_5 and L_{11} were the most effective against the tested microorganisms (diameter of inhibition zones were 7.3 ml) after three days,at the conc.250 ppm the inhibition % are 100 % (TABLE 6)[36].

CONCLUSION

- A new series of bisazo-dianils compounds were synthesized and characterized by different methods of analysis.
- From the biological activity studies,it was foun that these compounds cande used as anti-fungi.

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