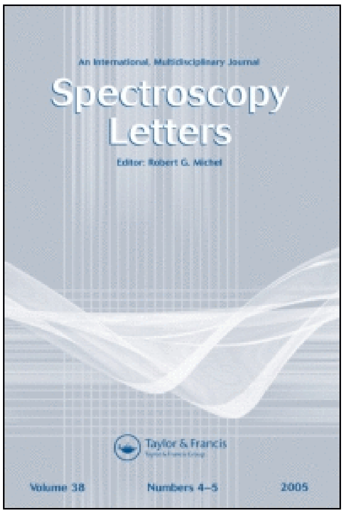

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NMR, Absorption and Fluorescence Parameters of Azlactones

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Nmr, absorption and fluorescence parameters of azlactones

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Abstract - Absorption and fluorescence wavelenghts for a series of azlactones have been measured from acetonitrile solutions that had no pre-light exposure. Fluorescence quantum yields, Q_F, are found to be in general less than 0.01, excluding the the derivatives with naphthyl and *p*-dimethylaminophenyl substituents. Previously reported Q_F values did not not fit to our results.

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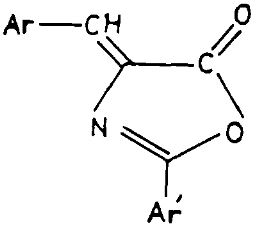
INTRODUCTION

2-Aryl-4-arylmethylene-5-oxazolones (azlactones) were first prepared at the beginning of century [1], and have been the subject of much attention since then for various applications. The preparation of addition polymers and polyamides from alkenyl azlactones and bisazlactones has been reported by Rasmussen *et al.* [2], while the use of azlactones as intermediates for biologically active peptides [3], as herbicides and fungicides [4], and as drugs pesticides and agrochemical intermediates has been widely studied [5]. Baese *et al.* have reported the use of of azlactones for the active site titrations of enzymes [6], they have been explored as antihypertensives [7] and they have been used for the asymetmetric synthesis of aminoacids [8]. Other important applications include their use in photosensitive compositions for semiconductor devices [9], electrophotographic photoreceptors [10], and organic non-linear optical materials [11].

In spite of wide range of applications of azlactones arising from luminescence behaviour and structural characteristics, there appear to be limited data on luminescence properties. The fluorescence behaviour of these compounds was first been reported by Eisenbrand in the solid and liquid state, with fluorescence bands at 480, 530 and 615 nm wavelengths [12]. Baumann noted two major photochemical processes of azlactones: hydrogen abstraction from solvent and geometrical isomerization [13]. Photodimerization of azlactones in benzene solutions at room temperature was reported by Adembri *et al.* [14]. Fluorescence re-absorption in sensizited reactions of azlactones has been examined by Sakuragi *et al.* [15]. These results indicate the photoinstability of azlactones in liquid state. Spectral fluorescence properties and some solvent interactions have been reported by Kravotiskii [16] and by Antonius [17], but the results of the two studies are not in agreement. The photoinstability of azlactones has been noted during photooxygenation studies [18], and recently Muneer *et al.* have carried out electron transfer reactions with azlactones [19] .

In view of the contradictory information presently avaible, we have restudied the absorption and emission characteristics of some azlactones to obtain accurate data. The azlactones 1-10 were prepared and fully characterised (see analytical and spectroscopic data in Tables 1-3).



Azlactone	Ar	Ar'
1	Phenyl	Phenyl
2	p-Anisyl	Phenyl
3	p-*N*,*N*-Dimethylaminophenyl	Phenyl
4	2-Furanyl	Phenyl
5	α-Tolyl	Phenyl
6	p-Chlorophenyl	Phenyl
7	α-Hydroxyphenyl	Phenyl
8	α-Tolyl	α-Tolyl
9	2-Hydroxy-l-naphthyl	Phenyl
10	2-Hydroxy-l-naphthyl	α-Tolyl

EXPERIMENTAL

IR spectra were recorded with an IFS 66 spectrophotometer and elemental analyses were obtained with a Carlo Erba 1106 C,H,N analyser. The proton and

Table 1. Melting points and analytical data for azlactones **1-10**

Compound	m.p.(°C)	Calculated %C	Calculated %H	Calculated %N	Found %C	Found %H	Found %N
1	71	77.71	4.42	5.62	76.82	4.29	5.64
2	159	73.12	4.66	5.02	73.08	4.56	4.97
3	214–5	73.97	5.48	9.59	74.16	5.39	9.53
4	175	70.29	3.76	5.86	69.94	3.61	5.97
5	142	77.57	4.94	5.32	77.54	4.86	5.44
6	172–3	67.84	3.53	4.94	67.84	3.41	4.91
7	144	72.45	4.15	5.28	72.18	4.09	5.02
8	150	77.98	5.42	5.05	78.09	5.31	4.96
9	235	76.19	4.13	4.44	76.08	4.03	4.44
10	240	76.60	4.56	4.26	76.61	4.26	4.10

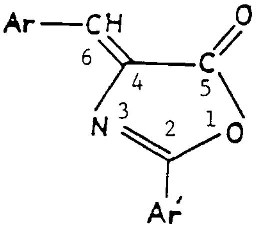
carbon-13 nmr spectra were taken with a Bruker 270 MHz instrument and UV absorption spectra with a Perkin Elmer 320, Lambda 5 spectrophotometer. A Spex Fluorolog spectrophotometer was used for emission spectra with a reference probe of 9,10-diphenylanthracene (9,10-DPA, Q_F=0.90) for fluorescence quantum yield measurements. The samples were deoxygenated with argon. Uvasol-Merck acetonitrile was used as solvent, and the fluorescence of the solvent was checked after completion of the fluorescence measurements.

The 2-aryl-4-arylmethylene-5-oxazolones (azlactones) were prepared by the cyclization of hippuric acid derivatives with the aromatic aldehydes in the presence of acetic anhydride. The hippuric acid derivatives were obtained by the reaction of aroyl chlorides and glycine. The azlactones were purified by crystallization, and identified in ir, nmr spectra and spectra and elemental analysis (see Tables 1-3).

Table 2. Proton NMR data of azlactones **1-10**

	Ar-CH=	CH3	OH	Aromatic Protons (Ar and Ar')
1	7.19(s)	-	-	7.43-7.61(m, 6H); 8.12-8.19(m, 4H)
2	7.16(s)	3.85(s)	-	6.96-(d, 2H); 7.45-7.59(m, 3H); 8.10-8.16(m, 4H)
3	7.19(s)	3.07(s);3.08(s)	-	6.71-6.75(d, 2H); 7.45-7.55(m, 3H); 8.11-8.16(m, 4H)
4	7.15(s)	-	-	6.63-6.55(m,1H); 7.47-7.58(m, 4H); 7.66-7.67(dd, 1H); 8.11-8.15 (m, 2H)
5	7.23(s)	2.51(s)	-	7.31-7.34(m,2H); 7.49-7.53(m, 3H); 7.57-7.59(m, 1H); 8.15-8.17(m, 2H); 8.76-8.78 (m, 1H)
6	7.12(s)	-	-	7.37-7.39(m, 2H); 7.50-7.63(m, 3H); 7.97-7.98(m, 1H); 8.14-8.17(m, 2H); 8.26(s, 1H)
7	7.30(m)	-	8.83(s)	7.30-7.33(m, 1H); 7.41-7.59(m, 5H); 7.89-7.91(d, 2H);8.82(s, 1H)
8	7.25(s)	2.52(s);2.81(s)	-	7.30-7.34(m, 4H); 7.45(m, 1H); 7.53(s, 1H); 8.07(d, 1H); 8.76(d, 1H)
9	7.68-7.69(m)	-	9.69(s)	7.45-7.47(d, 1H); 7.51-7.60(m, 4H); 7.88-7.96(m, 4H); 8.37-8.39(d, 1H); 8.90(s, 1H)
10	7.66-7.69(m)	2.58(s)	9.63(s)	7.27-7.30(m,2H); 7.38-7.44(m, 2H); 7.54-7.59(m, 2H); 7.87-7.89(d, 2H); 8.34-8.36(d, 1H); 8.50(s,1H)

Table 3. Carbon NMR data of azlactones **1-10**



	C-2	C-4	C-5	C-6	CH_3
1	163.4	133.4	167.4	131.1	-
2	162.3	130.9	167.8	131.7	55.3
3	160.5	128.3	168.5	132.2	39.9
4	162.9	130.4	167.0	120.1	-
5	163.7	133.2	167.8	128.6	20.0
6	164.3	134.8	167.2	131.8	-
7	158.9	133.5	166.0	125.2	-
8	163.8	133.2	167.7	128.3	20.0-22.8
9	158.9	133.6	166.2	126.3	-
10	158.6	134.8	168.7	126.2	20.1

2-o-Tolyl-1-o-tolylmethylene-5-oxazolone.

o-Toluic acid (3.0 g. 0.022 mol) was warmed with thionyl chloride (2.9 g, 0.024 mol) on a water bath for I h. *o*-Toluoyl chloride was distilled at 213°C and was used immediately. Glycine (0.75 g, 00.1 mol) was dissolved in 10 ml sodium hydroxide and *o*-toluoyl chloride (1.5 g, 0.01 mol) was added in portions with vigorous stirring. The solution was stirred for 0.5 h at room temperature then cooled to 0°C and was acidified with HCl. *o*-Toluoyl glycine was collected by filtration and washed with cold water. A mixture of *o*-tolylaldehyde (0.6, 0.005 mol), *o*-toluoyl glycine (1.0 g, 0.0005 mol), and sodium acetate (0.4 g, 0.005 mol) was heated with acetic anhdride (1 ml, 0.010 mol) on a water for 2 h. Then ethanol. (20 ml) was added while cooling and reaction mixture was allowed to stand overnight. The yellow crystalline product was collected by filtration washed with cold ethanol and recrystallized from chloroform-benzene. This gave 0.55 g (40%) of pure *2-o-tolyl-4-o-tolylmethylene-5-oxazolone*, mp 150°C.

RESULTS AND DISCUSSION

The UV spectra of the azlactones **1-10** were measured with fresh acetonitrile solutions, and care was taken to minimize exposure to light. We have observed similar result for the variation of bands above 300 nm, as reported by Adembri [14] for the cause of photodimerisation (Figure 1). All the acetonitrile solutions of azlactones began to show lower absorptions and emmisions after several hours of daylight irradiation. The enhancement of band intensities about 240-280 nm was, accompanied by adecline of bands above 300 nm. Deoxygenation of samples did not modify these observations.

Table 4 gives the lists of absorbance parameters from minimal photodisturbed azlactones. The maximum absorption is seen for λ_2 bands. This band absorbs about 360-380 nm, excluding **3** and **7**, which have absorption

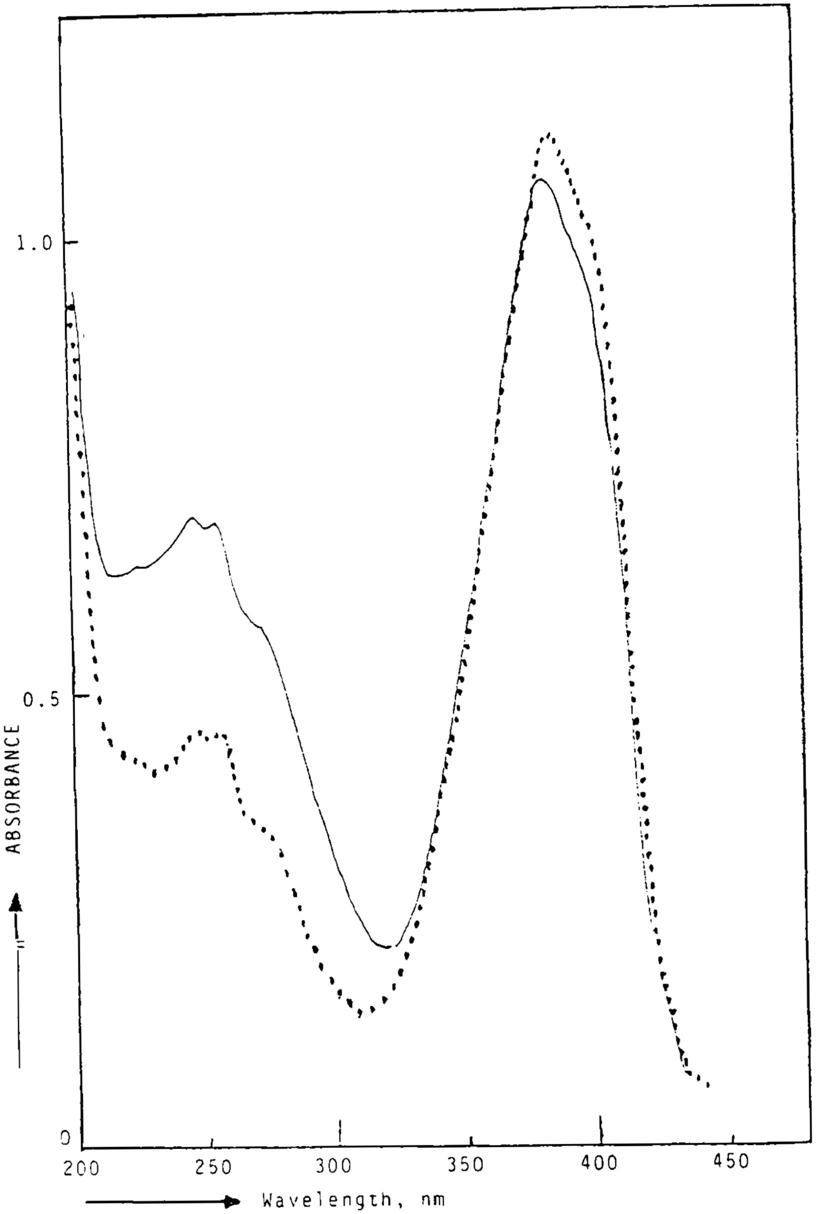


Fig. 1. The absorption spectra of azlactone 2 in acetonitrile; a) (....) fresh solution, b) (——) after six hours of daylight irradiation at room temperature.

Table 4. The UV absorption data of azlactones in acetonitrile.[a,b,c]

Compound	$\lambda_1(\varepsilon_1)$	$\lambda_2(\varepsilon_2)$	$\lambda_3(\varepsilon_3)$	$\lambda_4(\varepsilon_4)$	$\lambda_5(\varepsilon_5)$	$\lambda_6(\varepsilon_6)$	$\lambda_7(\varepsilon_7)$	$\lambda_8(\varepsilon_8)$
1	381(4.0)	362(5.8)	346(4.1)	262(1.9)	249(1.6)	239(1.4)		
2	401(3.2)	382(3.6)		279(2.8)	261(1.3)	246(1.2)		
3		465(5.1)		301(1.0)		242(1.2)		
4	403(3.3)	384(3.6)			264(1.2)			
5	388(2.7)	367(3.0)	350(2.5)	261(1.3)	250(1.3)	242(1.2)		
6	380(1.8)	359(2.6)	342(2.0)	261(1.5)	250(1.5)	242(1.4)		
7	337(1.7)	324(2.3)	312(2.0)	302(1.7)	259(0.7)	248(1.0)	238(1.3)	
8	384(2.5)	364(3.2)	345(2.6)	261(1.4)	249(1.3)	241(1.2)		
9	371(2.1)	355(2.4)	325(1.4)	312(0.9)	298(0.7)	264(1.4)	237(4.1)	230(4.1)
10	374(1.6)	355(2.0)	325(1.3)	312(0.9)	298(0.6)	264(1.2)	237(4.4)	230(3.4)

[a] At concentrations of (1–3) x 10^{-5} M; [b] λ (nm); [c] $\varepsilon \times 10^4$ ($M^{-1}cm^{-1}$).

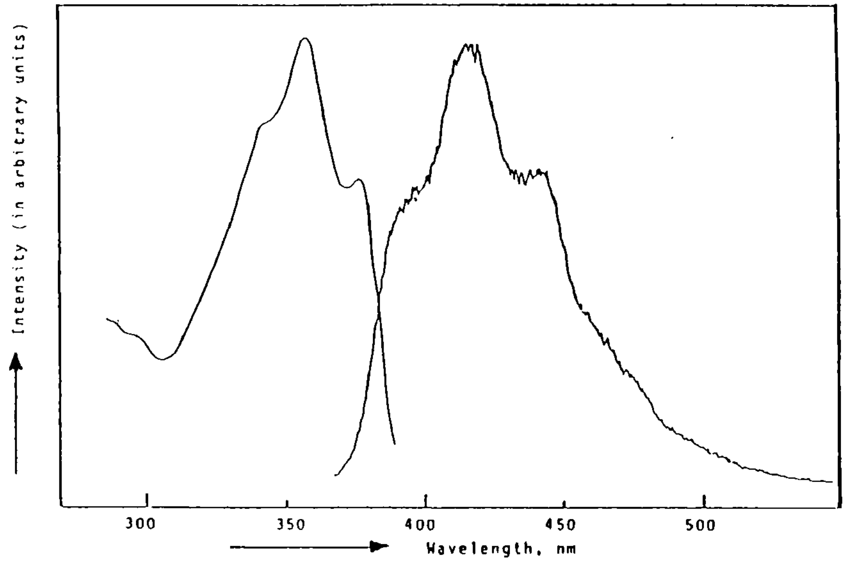


Fig. 2. The absorption and emission spectra of azlactone **6** in acetonitrile at room temperature, λ_{exc}=359 nm.

maxima at 465 and 324 nm, respectively. These variations may be attributed to enhanced conjugation in **3** and lower conjugation in **7**, which would alter the π-π^* transitions corresponding to wavelengths above 300 nm.

The room temperature absorption and emission spectra of azlactone **6** are shown in Figure 2. Emission spectra were recorded at excitation wavelengths corresponding to the λ_2 bands (Table 5). Emission band intensities were found to be unaltered by deoxygenation on argon purged solutions. As reference probe for fluorescence quantum yield measurements, 9,10-diphenylanthracene (9,10-DPA, λ_{max} = 371.5 nm) was used. The absorption and emission spectra of 9,10-DPA were recorded in deoxygenated hexane solutions, and a correction factor from acetonitrile to hexane is included in the calculations. Table 5 gives the calculated

Table 5. The emission data and the fluorescence quantum yields of azlactones in acetonitrile.[a]

Compound	λ^b_{exc}	λ^{max}_{fl}	Q^c_F	Q^{lit}_F
1	362	416	0.002	0.01[16]
2	382	460	0.001	0.08[17]
3	465	543	0.012	0.01[16] $1.6 \times 10^{-4} - 4 \times 10^{-3}$[17]
4	384	440	0.001	
5	367	427	0.001	
6	359	416	0.004	
7	324	397	0.002	
8	364	417	0.002	
9	355	423	0.033	
10	355	415	0.116	

[a] At concentrations of (1–3) x 10^{-5} M. [b] Excitations at maximum absorption bands above 300 nm. [c] Error limits are estimated to be ± 10%.

fluorescence quantum yields together with the fluorescence wavelength bands. The fluorescence quantum yields reported by Krasovitskii[16] and Antonius[17] are inconsistent. The extremely low fluorescence quantum yields reported for azlactone **3** by Antonius (Q_F is 4 x 10^{-3} and 1.6 x 10^{-4}, glycerol and benzene, respectively) is understandable. We had observed a Q_F of 2 x 10^{-3} for **3**, after eight hours of daylight radiation in acetonitrile. The light-exposed solutions of other azlactones gave fluorescence quantum yields 10-100 times less than solutions kept in the dark. It is difficult to understand the higher Q_F values for the azlactones **1** and **2**, 0.01 and 0.08, respectively, as reported by Krasovitskii *et al.* [16].

As seen from Table 4, substituents on the aromatic rings did not alter the fluorescence quantum yields, except for compounds **3, 9** and **10**. It is known [16] that *p*-dimethylamino substitution on aromatic rings and condensed aromatic rings gives gives high fluorescence. This explains the enhanced Q_F of 0.012 in **3** and Q_F of 0.033 and 0.116, in **9** and **10**, respectively, with 1-naphthyl substitution. The influence of naphthyl substitution on fluorescence quantum yields has also been observed in perylene diimide derivatives [20].

CONCLUSION

Overall, our results show that light sensitive solutions of azlactones must be handled by taking due precautions towards light exposure for spectral measurements. In general, azlactones give low fluorescence quantum yields. The fluorescence of the 5-oxazolone ring increases with substituted aryl groups which already have emmision characteristics.

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