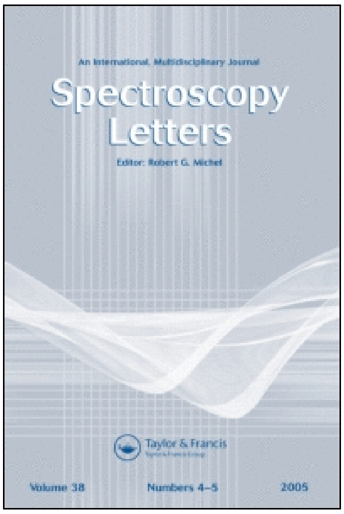


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Structure and Luminescent Properties of the 4-Arylidene-2-Aryl-5-Oxazolones(Azlactones)In Solution and Crystalline State

S. Icli[a]; A. O. Doroshenko[b]; S. Alp[a]; N. A. Abmanova[b]; S. I. Egorova[b]; S. T. Astley[a]
[a] Department of Chemistry, Faculty of Science, Ege University, Bornova, Izmir, Turkey [b] Institute for Chemistry at Kharkov State University, Kharkov, Ukraine

To cite this Article Icli, S. , Doroshenko, A. O. , Alp, S. , Abmanova, N. A. , Egorova, S. I. and Astley, S. T.(1999) 'Structure and Luminescent Properties of the 4-Arylidene-2-Aryl-5-Oxazolones(Azlactones)In Solution and Crystalline State', Spectroscopy Letters, 32: 4, 553 — 569

To link to this Article: DOI: 10.1080/00387019909350006

URL: http://dx.doi.org/10.1080/00387019909350006

SPECTROSCOPY LETTERS, 32(4), 553–569 (1999)

STRUCTURE AND LUMINESCENT PROPERTIES OF THE 4-ARYLIDENE-2-ARYL-5-OXAZOLONES(AZLACTONES) IN SOLUTION AND CRYSTALLINE STATE

KEYWORDS: Azlactones, fluorescence emission, fluorescence quantum yields, quantum chemical calculations, fluorescence lifetimes, excited state intramolecular proton transfer.

S. Icli[a,*], A.O. Doroshenko[b], S. Alp[a], N.A.Abmanova[b], S.I.Egorova[b] and S.T.Astley[a]

[a] *Department of Chemistry, Faculty of Science, Ege University, 35100 Bornova, Izmir TURKEY*
[b] *Institute for Chemistry at Kharkov State University, 310077 Kharkov UKRAINE*

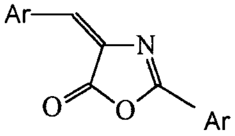
ABSTRACT

Experimental and theoretical evaluations have proven that very low fluorescence quantum yields of azlactones in solution are not caused by an efficient inter system crossing from $S_1{}^*(\pi\pi)$ to $T^*(n\pi)$ states, but rather from solvation and steric effects, that result in non-planarity of the molecular system. High fluorescence quantum yields in the solid state are attributed to the planarity of the azlactone molecule upon packing into the crystal lattice. Supporting evidence was found upon observation of the excited state proton transfer (ESIPT) bands of fluorescence emissions of *o*-hydroxyarylidene derivatives. The photoinstability of azlac-

tones in liquid states are attributed to photochemical E-Z isomerization and cleavage of the hetero ring α to the carbonyl group.

1. INTRODUCTION

Derivatives of 4-arylidene-2-aryl-oxazolone-5 (azlactone) have been extensively studied as a precursor to some organic compounds, such as amino acids[1], amide containing polymers[2,3] and a wide range of biologically active compounds[4-7]. Various photochemical applications of azlactone derivatives are also seen in the literature[8-10]. Luminescent properties have been investigated by several authors[11-15], and very low fluorescence efficiencies have been reported for them in solutions with solvents of different nature. Considerable disagreements of data, as reported by different investigators appear in the literature[11-13]. The solid-state fluorescence emission of the aryl derivatives of 5-oxazolones were found to be much higher in comparison to the liquid state[12], but no conclusions were drawn for the photophysical parameters of azlactones in connection to the molecular structure. In this article we have investigated the fluorescent properties of some azlactone derivatives in solutions and solid states, and have tried to examine the correlation between the molecular structures and some basic characteristics of primary photophysical-photochemical processes arising from electronic excitations. The following derivatives of 4-arylidene-2-aryl-oxazolone-5 (azlactones) were selected for our investigations:



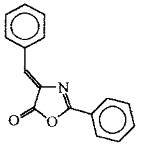
	Ar	*Ar'*
I	Phenyl	Phenyl
II	*p*-Anisyl	Phenyl
III	*p*-N,N-Dimethylaminophenyl	Phenyl
IV	*o*-Hydroxyphenyl	Phenyl
V	2-Hydroxy-1-naphthyl	Phenyl
VI	2-Hydroxy-1-naphthyl	*o*-Tolyl

2. EXPERIMENTAL

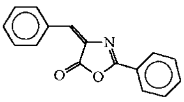
The synthesis, purification and spectral characterization of the studied compounds were reported earlier[16]. The electronic absorption spectra were measured on UV-1601 Schimadzu and Hitachi U3210 spectrophotometers, fluorescence excitation and emission spectra were determined on PTI QM1 and Hitachi F4010 fluorescence spectrometers. The fluorescence quantum yields were determined relative to the methanolic solution of anthracene (φ_f=0.249), for which quantum yield was previously measured with a quinine sulfate in 0.5 M H_2SO_4 solution (φ_f=0.546) as a reference standard[17]. The fluorescence kinetics and time-resolved spectra were measured on the nanosecond pulse fluorometer, working with single-photon timing mode in the nanosecond range, as described by Doroshenko et al[18].The samples for fluorescence measurements in the crystalline state were prepared by the evaporation of concentrated solutions of azlactones in acetone on a quartz plate. The wavelengths close to the absorption maxima in acetonitrile solutions were used for the excitation of fluorescence. Quantum-chemical calculations with the optimization of the molecular geometry were made by the semiempirical method AM1[19] using MOPAC 6.0 program; the electronic spectra were calculated by the π-electron method PPP CI, updated by the procedures of calculations of special indices-electronic localization and charge transfer numbers[20] using EASY-PI program and a set of parameters as shown by Griffits[21].

3.RESULTS AND DISCUSSION

The literature X-ray structural data[22-24]our quantum-chemical calculations shows that the azlactone molecule would exist mainly in its Z-conformation:



Z



E

The energy of the E-isomer, calculated within the frames of the AMI method[19] are found to be higher than the Z-isomer, by more than 2 kcal/mole. This is not a high difference between the isomers, but however the height of the potential barrier between the Z and E isomers, would probably be higher. The existence of a high potential barrier between these two isomers may be qualitatively confirmed by a possible transformation of one into another only on a photochemical path[9]. The theoretical calculations of the Frank-Condon triplet state of the azlactone molecule shows the existence of considerable excess of spin density on the methylenic C=C double bond at position 4 of the oxazolone ring. The photochemical activity of the azlactones in their excited triplet state could be determined by the transformations related to the methylenic double bond. Our calculations show that, the order of this bond in the T_1*-state is considerably reduced. Thus an increase in C=C bond length of the planar conformation of the triplet state occurs(from 1.35 A° in the ground state to the 1.45 A° in the "flat" lowest triplet). The calculations, carried out with the full optimization of molecular geometry in the lowest triplet state of the azlactone molecule showed that intramolecular rotation about the methylenic C=C bond occurs. This results in the formation of the so-called ‘twisted triplet’ state, typical for most ethylenic compounds. Thus, upon returning to the ground state, both Z and E isomers can be formed from the energetically unfavorable twisted conformation with approximately equal probability. Therefore, we can assume that the photochemical Z-E isomerization from the triplet state is the main photoprocess, typical for all the derivatives of azlactones.

Another site of photochemical activity is on the C-O single bond α to the carbonyl group in the oxazolone ring, which is another point of localization of increased spin density in these molecules. This photochemical activity, connected with the cleavage of the azlactone ring is expected to occur for the above azlactone derivatives. The evidences in favor of this conclusion can be seen in the literature[25]. Krasovitskii, Icli and other authors have reported very low fluorescence quantum yields of azlactones, $Q_f<0.01$, in solution[11-16]. Intersystem crossing from $S_1*(\pi\pi)$ to $T*(n\pi)$ states is reasoned as a main cause of low fluorescence quantum yields of azlactones. Our data, presented in table 1, presents the low fluorescence quantum

TABLE 1

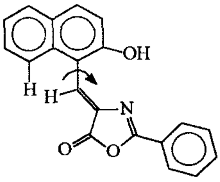
The spectral properties of studied azlactones in methanol and acetonitrile.

Comp.	Solvent	ν_a, cm^{-1}	λ_a, nm	ν_f, cm^{-1}	λ_f, nm	$\Delta\nu_{ST}$, cm^{-1}	φ_f
I	Methanol	27820	360	22720	440	3400	0.0002
	Acetonitrile	27780	360	24080	415	3700	0.0001
II	Methanol	26120	383	22560	443	3560	0.0006
	Acetonitrile	26180	382	22460	445	3720	0.0007
III	Methanol	21540	464	18460	542	3080	0.0018
	Acetonitrile	21500	465	18270	546	3230	0.0027
IV	Methanol	25540	392	22480	445	3060	0.0005
	Acetonitrile	27600	362	-	-	-	-
V	Methanol	28020	360	24460	408	3560	0.0072
	Acetonitrile	28160	355	24500	408	3660	0.0071
VI	Methanol	28160	355	24080	415	4080	0.0234
	Acetonitrile	28260	354	24500	408	3760	0.0199

yields, in agreement with previous results, but the cause of intersystem crossing from $S_1^*(\pi\pi)$ to $T^*(n\pi)$ states is questionable.

A principal role of intersystem crossing for the quenching of fluorescence emissions[15] does not appear to occur with all the derivatives as seen from table 1. The energy of the $S^*(n\pi)$ state of azlactones were evaluated to be near 33000 cm^{-1} by Krasovitskii[15]. Thus, the energy of the correspondent $T^*(n\pi)$ state should not be located lower than 29000-30000 cm^{-1}, taking into account the fact that S-T splitting of the $n\pi^*$ levels for intersystem crossings usually does not exceed 2000-3000 cm^{-1}. The energy of the lowest excited singlet state, even for the unsubstituted azlactone, **I**, (ref. 16 and table 1) is about 2000-2500 cm^{-1} lower than the energy of the estimated $T^*(n\pi)$. In such a case the intersystem crossing, which assumed to concur with the fluorescence emission, needs thermal activation. It seems to us that the efficiency of the mentioned thermally activated intersystem crossing process under such conditions (with a height of activation barrier of 2000-2500 cm^{-1}) could not be enough for a practically complete quenching of fluorescence. A good example is the dimethylamino substituted compound, **III**, where the energy of the S_1* state is about 21500 cm^{-1}, but still the fluorescence efficiency is very low, Q_f= 0.002-0.003. We can thus propose that the main reason of such a low fluorescence ability within the azlactone series, is not only the intersystem crossing, but possibly some photochemical diabatical process that acts in the excited singlet state, and is followed by a reverse reaction into the ground state. Such a reversed process of the lactone ring cleavage for various alkyl- and hydroxy- derivatives of coumarine was proposed by some authors, justifying the low fluorescent efficiency of these compounds in neutral solutions[26].

There may be some indirect approaches to the above proposal. The compounds **V** and **VI**. are the most efficiently fluorescent ones in our series of azlactones as seen in table 1 and as reported earlier[16]. This fact seems to be totally inconsistent with the statement, that the main reasonfor low fluorescent ability of azlactones is the intersystem crossing with the participation of T*(nπ) levels, because the energy of the S_1* state for both naphthalenic compounds are close to those of the unsubstituted azlactone derivative **I**. In principle the analogous positions of the energetic levels of ππ* and nπ* at **V** and **VI** are similar to **I** , but they differ in fluorescent efficiency by up to 70-100 times (table 1 and ref. 16). This result may be explained by an examination on the molecular structures of compounds **V** and **VI**. These molecules are expected to be planar, and their planar conformation should be stabilized by an intramolecular hydrogen bond between the hydroxy group in the 2-position of the naphthalene moiety and the nitrogen atom of the 5-oxazolone ring.



However, our calculations for the compounds **V** and **VI**, with an optimization of their geometry show that steric hindrance between the 8-hydrogen of the naphthalene ring and the hydrogen belonging to the methylenic C=C double bond at position 4 of the oxazolone ring, causes an out of plane twist between the naphthalene and the hetero ring systems. Our theoretical calculations indicates a dihedral angle of up to 55-60° is present in the azlactone molecules of **V** and **VI** . As a result, the distance between the proton-donor and acceptor group increases in comparison with the hypothetical planar conformation. Thus formation of an intramolecular hydrogen bond is unlikely to occur. For agreement, the measured IR spectra for **V** and **VI**, in the solid and liquid states confirm our theoretical calculations (table 2). The most striking results are seen in the vibration frequencies of O-H, C=O, C=C and ring C=N bonds.

The sharp single bands of valent vibrations of OH groups were observed both in the crystalline states and in solutions. The shift differences between solutions and solid states for ν_{OH} frequencies are 42 and 65 cm^{-1} in **IV** and **V**, respectively. This result may be attributed to weakening of hydrogen bonding interaction from solid state to solution. The intense bands of valent vibrations from the carbonyl, C=O, bond appear in the range 1710-1750 cm^{-1} in the solid state and solution for **IV** and **V** (table 2). They are accompanied by bands of comparable intensity from methylenic C=C double bond, that is highly polarized by the neighbouring polar carbonyl and C=N bonds, and appear at about 40-50 cm^{-1} lower frequencies than the carbonyl band. Frequency differences of both carbonyl and methylenic bonds from solution to solid state are twice as high going from **V** to**IV**, 30-33 cm^{-1} to 15 cm^{-1}, respectively. This result may be attributed to enhanced steric repulsions in azlactone **V**, where the aryl moieties are 2-hydroxynaphthyl and phenyl, instead of 2-hydroxynaphthyl and phenyl in azlactone **IV**. Additional steric hindrance caused by the *o*-tolyl moiety may have decreased the conjugation of the carbonyl and olefinic bonds. A most interesting result is seen on imino, C=N, group frequencies, upon comparison of compounds **IV** and **V** in table 2. Imino vibrational frequencies of azlactones are reported to be in the range of 1510-1580 cm^{-1} [16,17]. The nitrogen

TABLE 2

The infrared spectra data for azlactones **IV** and **V** in solid state and solutions (ν; cm^{-1}).

Compound	Group	Solution in CCl_4	Solid state, KBr	$\Delta(CCl_4\text{-}KBr)$
IV	OH	3410	3368	42
	C=O	1728	1713	15
	C=C	1687	1668	15
	C=N	1523	1533	-10
V	OH	3406	3339	65
	C=O	1741	1711	30
	C=C	1697	1664	33
	C=N	1567	1528	39

atom in the imino group is expected to be involved in a hydrogen bonding interaction with the hydroxyl group. Azlactone **V**, presents a decrease in hydrogen bonding in solution ($\Delta\nu_{CN}$ = 39 cm^{-1}), compared to the solid state. But the difference between liquid and solid states for the same frequencies is even slightly reversed for azlactone **IV**($\Delta\nu_{CN}$ = -10 cm^{-1}). This result also shows that azlactone **V** is less flattened compared to azlactone **IV**, because of steric hindrance of the *o*-tolyl moiety, that results in weaker intramolecular hydrogen bonding.

A further evidence for minimal intramolecular hydrogen bonds in azlactones of **IV** and **V** is seen by the absence of the excited state proton transfer (ESIPT) reaction. ESIPT is detected by appearance of a fluorescence emission band in the long-wavelength region, belonging to the product of ESIPT-excited phototautomer form. In contrast to compounds **V** and **VI**, the ESIPT reaction is observed in solvents of low polarity ($CHCl_3$) for compound **IV**, that have none or less steric hindrance for intramolecular hydrogen bonding interaction.

In order to clarify the nature of the chromophoric fragment, which makes a main contribution to the formation of the long-wavelength electronic transition, and in relation to determine the nature of the S_1*-state for azlactones **V** and **VI**, we have made a set of calculations by the π-electron PPP CI method,. The intramolecular rotation was modeled by the decreasing of the semiempirical bond parameter - overlap integral β_{ij} proportional to the cosine of the correspondent dihedral angle. It follows from the results of the latter calculations that the lowest excited singlet states of azlactones **V** and **VI** are localized on the naphthalene ring, and are close by nature to the corresponding excited state of α-substituted β-naphtole. In such a case, the efficiency of the proposed above reversed photochemical process has to be lower, and an increase on fluorescence quantum yield should be observed as seen for azlactones **V** and **VI** in table 1.

Investigations of emission spectra of azlactones **I-VI** in acidic media also demonstrates the presence of a fast photochemical transformation that would cause the very low fluorescence quantum yields. A very rapid photochemical reaction, that led to the practically complete disappearance of the optical density at the excitation wavelength, 365 nm, was observed for the azlactones **I-III**. The rate of this reaction was so significant, that even no emission spectra could be measured for azlactones **I** and **II** in acidified methanol solutions. One may make an assumption from these results that the protonation in acidic media stabilizes the products of the photochemical transformations making the reaction irreversible, which is reversible in neutral solutions. The isolation and identification of the photoproducts of azlactones in acidified alcoholic solutions and further studies on acid-base interactions can lead to a greater understanding of the nature of the above postulated photoprocess.

However it is well-known that azlactones have practically no fluorescence in solution, but show intense emissions in the crystalline state[12]. In spite of these observations, there are very few literature data available for solid state fluorescence luminescence of azlactones. A direct measurement could not be done, because, an unhomogeneous poly-crystalline surface prevented the consistency of optical density measurements. However, the solid state quantum efficiencies have been evaluated from the spectral data in solutions by approximations(k_f - fluorescence rate constant, calculated from the absorption spectra in acetonitrile according to a formula in the literature[27], that takes into account the shape of the first absorption band, separated mathematically from the full spectrum) and for fluorescence kinetic data of the solid state (τ_f - solid state fluorescence lifetimes), according to the equation of:

$\varphi_f = k_f \tau_f$. The results of these calculations are shown in table 3.

The quantum efficiencies are seen to be very high, exceeding the corresponding values in solution tenfold to a thousandfold times. Such an improvement of fluorescence emission is difficult to explain. One can point out that azlactone molecules are more planar and more rigid, without any intramolecular rotations in the crystalline state, compared to the solutions. Another additional factor for the enhancement of Q_f values in the solid state is, the cleavage of the azlactone ring, which must be much less probable in the crystalline structure.

The quantum yield of dimethylaminophenyl azlactone, **III**, was found to be near to 1.0, because the reciprocal value of the lifetime ($1/\tau_f = 1/5.09$ ns $= 1.98 \cdot 10^8$ s^{-1}) is less than the calculated k_f value, $3.08 \cdot 10^8$ s^{-1}, from the absorption spectrum in acetonitrile. Such a discrepancy would occur, because the true k_f value of azlactone **III** in crystalline state would differ from the k_f value in solution. An interesting result is seen with the *ortho*-hydroxyl derivatives of **IV** and **V**. As explained above, the excited state intramolecular proton transfer reaction (ESIPT) is typical for conjugated compounds with intramolecular hydrogen bonding in solution. The ESIPT reaction is the main reason for the observed two-band fluorescence spectrum of azlactones **IV** and **V** in chloroform solutions. The long-wavelength fluorescence band belongs to the emission of the phototautomer, which do not exist in the ground state. The energy of the phototautomer is less compared to the "normal" Frank-Condon form, so the Stokes shift value is usually considered as "abnormally high".

TABLE 3

Fluorescence properties and photophysical parameters of azlactones in the solid state.

(The data for compounds IV and V were obtained from time resolved spectra)

Comp.	*Ar*	ν_f, cm^{-1}	λ_f, nm	τ_f, ns	k_f, s^{-1} (x10^8)	Q_f
I	Phenyl	21320	469	0.138	4.67	0.064
II	p-Anisyl	19220	520	0.702	4.62	0.32
III	p-N,N-Dimethyl aminophenyl	16540	605	5.06	3.08	(~1.0)
IV	o-Hydroxyphenyl	25060 23160	399 432	0.757 2.007	5.09	see text
V	2-Hydroxy-1-naphtyl	21980 20780	455 481	2.015 5.263	2.10	see text

The unusually wide emission band of compound **IV** in the crystalline state, attracted our attention. In order to clarify such a behavior, we have measured the time-resolved fluorescence spectra of *o*-hydroxyphenyl azlactone in the solid state. The results are presented in figure 1. One observes two emitting components, first of which corresponds to the "normal emission" of **IV**, and the second may be attributed to the fluorescence of the phototautomer. The phototautomer form does not exist in the ground state, so its emission appeared with a short delay after the beginning of the excitation. Consequently, the emission of the normal form, which produces the phototautomer as a result of the ESIPT reaction, disappears more quickly in comparison to the tautomer.

The ESIPT rate constant could be evaluated from the fluorescence quantum yield and kinetic data according to the following considerations[28]. Let us consider the general scheme of the ESIPT process:

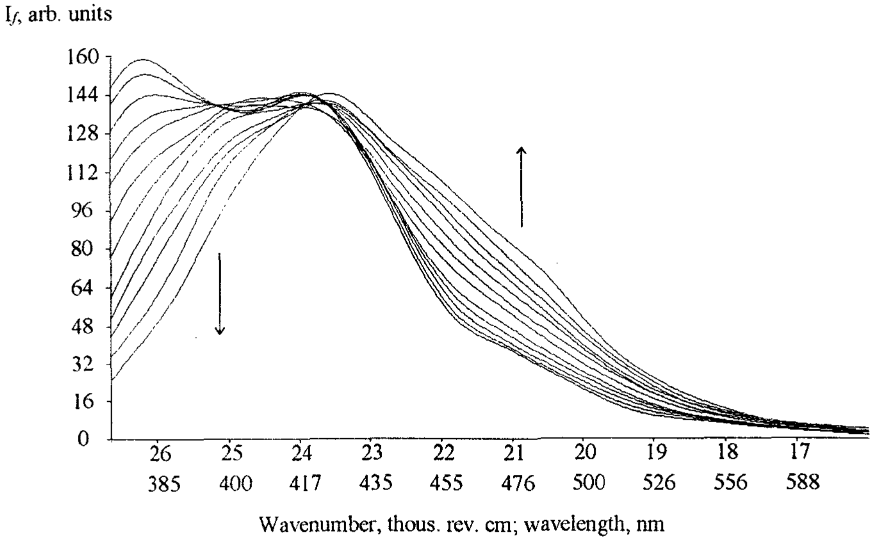
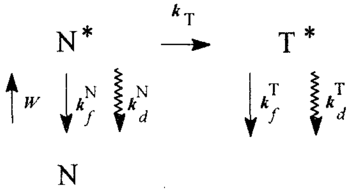


FIG. 1. The time-resolved fluorescence spectra of compound **IV** in the crystalline state with a time interval of ~5 ns.



N and *T* corresponds to the normal form and phototautomer, respectively, k_f and k_d are the kinetic constants of fluorescence emission and the radiationless degradation, respectively. k_T corresponds to the rate of the ESIPT reaction, and *W* is the optical excitation. The following formula for the quantum yields of the normal form and phototautomer form can be deduced under the photostationary conditions.

$$\varphi_N = \frac{k_f^N}{k_f^N + k_d^N + k_T} \qquad (1)$$

$$\frac{\varphi_N}{\varphi_T} = \frac{k_f^N}{k_f^T} \cdot \frac{k_f^T + k_d^T}{k_T} \qquad (2)$$

The equations for evaluation of kinetic constants for the primary photoprocesses of ESIPT, can be obtained from the equations (1) and (2):

$$k_T = \frac{k_f^N}{k_f^T}\frac{\varphi_T}{\varphi_N} \times (k_f^T + k_d^T) = \frac{k_f^N}{k_f^T}\frac{\varphi_T}{\varphi_N} / \tau_T \qquad (3)$$

$$k_d^{N,T} = 1/\tau_{N,T} - k_f^{N,T} \qquad (4)$$

The k_f^T value of the phototautomer, that is necessary for the evaluation of the ESIPT kinetic constant, can not be obtained from any experimental data, because the phototautomer does not exist in the ground state. Therefore the k_f^T value is being set to be close to the corresponding k_f^N value of the "normal" form. This assumption is crude, but the close proximity of the ESIPT rate constant values, obtained by the two methods discussed above (eq. 3) and by a more complicated one (in reference 18 the full surface of fluorescence decay is taken into account), justifies the applicability of the above assumption to the present case in general, see equations (3) and (4).

The rate of the ESIPT process for the *o*-hydroxyphenyl azlactone, **IV**, in the crystalline state, is k_T(**IV**) = $7.85\cdot10^8$ s^{-1}, which is rather low in comparison with the usual proton photo-transfer rates[29]. The most probable reason for this observation may be the low basicity of the proton-accepting center, that is the nitrogen atom of the azlactone ring. The electron withdrawing carbonyl group has to be the cause of the low basicity of the azlactone nitrogen.

An interesting observation was the near absence of radiationless degradation in the "normal" form: $k_d^N = 1/\tau_f^N - k_T = 2.7\times10^7$ s^{-1} in the solid state. This low value is typical of very efficient luminophores. However, near non-existence of intramolecular quenching in the phototautomer should be noticed ($k_f^T \approx 1/\tau_f^T \sim 5\cdot10^8$ s^{-1}, that is assumed to be close to the related k_f^N value in our calculations). According to our previous investigations of the *ortho*-hydroxy derivatives of 2,5-diphenyloxazole, which exhibited ESIPT, the radiationless deactivation in the phototautomer form is the most efficient and it is the main reason for the total low intensity of fluorescence in such systems[28].

The results of the theoretical evaluation of azlactone **IV** indicated the neccessity of a time-resolved fluorescence study on 2-hydroxy-1-naphthyl azlactone, **V**. The ESIPT reaction was not observed for this compound in solution. In contrast, the time resolved fluorescence spectra of **V** was found to display similar behaviour to **IV** in the solid state (figure 2).

The value of the ESIPT rate constant of **V**, was calculated to be k_T (**V**)=$2.33\cdot10^8$ s^{-1}.In comparison to the rate of ESIPT in azlactone **IV**, it is about threefold lower. The low efficiency of the radiationless dissipation of the energy of electronic excitation in both, normal form and phototautomer, is also seen in the azlactone **V**. The probable reason for such a different behavior of **V** in the crystalline state with respect to solutions, may be the flattening of the sterically hindered molecule while packing into the crystalline lattice, that promotes the approachment of the proton-donor and proton-acceptor groups in the solid phase, and results in the ESIPT process in solid state.

4.CONCLUSIONS

- The considerable increase of fluorescent intensity in the solid state compared with solutions, can be explained by a flattening of the azlactone upon packing into the crystal lattice, and consequent prevention of any intramolecular rotations and movements.

- Investigations on acidified solutions of azlactone derivatives have shown a rapid photochemical reaction, that leads to the destruction of the conjugated system of the 5-oxazolone ring and results in considerable short-wavelength shift in the absorption spectra.

- The low efficient excited state proton transfer reaction (ESIPT) with kinetic rate constants in the order of 1×10^8 s^{-1} was observed for the *o*-hydroxyaryl azlactones **IV** and **V**, in the crystalline state. It is shown, that this solid state ESIPT reaction was not followed by the radiationless decay of the energy of the electronic excitation, typical to the molecules that exhibit ESIPT in solutions.

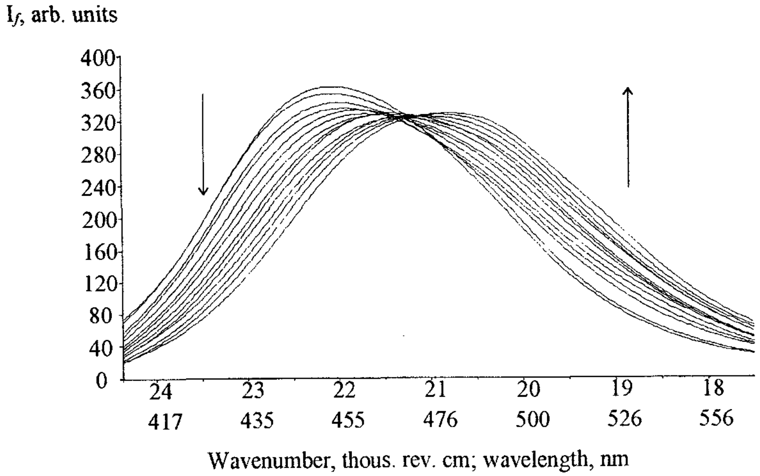


FIG. 2. The time-resolved fluorescence spectra of compound **V** in the crystalline state with a time interval of ~9 ns.

- Quantum-chemical calculations show possible reasons for the photochemical instability of the derivatives observed in the azlactone series; a) the photochemical Z-E isomerization around the methylenic C=C bond at position 4 of the heteroring and, b) the cleavage of the azlactone ring at the α-position to the carbonyl group.

ACKNOWLEDGEMENTS

Authors thank to NATO Scientific Affairs Division, TUBITAK(Scientific and Technical Research Council of Turkey) research grant TBAG-1564 and Ege University Research Funds Office for supports.

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Date Received: January 6, 1999
Date Accepted: April 19, 1999