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Synthesis, photophysical and photochemical properties of oxazolone derivatives

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Acyloxyphenyl derivatives of oxazolone, which have tree photo active centers, were synthesized and their physicochemical properties are determined by NMR, absorption, fluorescence excitation and emission spectroscopies. The semi-empirical calculations carried out according with the theory of the PM3/CI level has shown, that at an irradiating of their solutions by UV-light give no possibilities of the photo-Fries reaction. The calculated values are in a good accordance with the experimental ones.

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Keywords: Oxazolone, Luminescent properties, Photo-Fries rearrangement

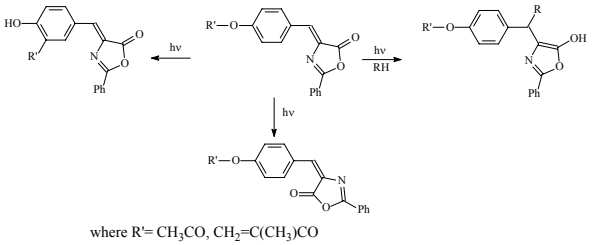
1. Introduction

Benzene oxazolones and their analogs are known for their biological properties [1-3]. Compounds with oxazolones ring exhibit antibacterial [4] as well as antifungal activities and show a wide range of pharmaceutical properties [5].

On the other hand these molecules are interesting due to their important photophysical properties [6-9]. The classical Erlenmeyer azlactone synthesis [10] is an important method for preparing aromatic amino acids [11-14]. Established the Erlenmeyer azloctone synthesis [15-17] is a well known reaction that is widely applied for the preparation of 2-aryl- (alkyl-) 4-arylmethylene-2-oxazolin-5-ones. This reaction consists in heating aromatic aldehydes with hippyric or aceturic acids in the presence of acetic anhydride and sodium acetate. The next development in the part of preparation and investigation properties of compounds based on oxazolones was done to describe photochemical and photophysical properties of these compounds [18, 19].

The photo-Fries reaction has been investigated extensively since the discovery of the reaction by Kobsa [20] and Anderson and Reese [21]. Several review papers on the reaction have been published [22, 23]. The scope of the reaction has been extended from phenyl esters and phenyl carbonates to include other compounds containing the phenoxy group, such as phenoxyacetic acid [24], acetanilides [25], phenyl ethers [26], and hydroxyphenyl cinnamates [27]. All available evidence on the mechanism of the photo-Fries reaction suggests that the rearrangement is intramolecular. It has been demonstrated that the relative quantum yields for the formation of o- and p-hydroxyphenone groups from solid poly (phenylacrylate) via the photo-Fries rearrangement reaction do not depend on the temperature and the wavelength of excitation [27].

Thus for the ethanol solution of phenyloxazolone derivatives the next phototransformations are possible:



2-Phenyl-4-[[4-acetyloxyphenyl]methylene]-5(4H)-oxazolone (IIIp), 2-phenyl-4-[[3-acetyloxyphenyl]methylene]-5(4H)-oxazolone (IIIm), 2-(benzoylamino)-3-(4-hydroxyphenyl)-2-propenoic acid (IVp), 2-(benzoylamino)-3-(3-hydroxyphenyl)-2-propenoic acid (IVm), 2-phenyl-4-[(4-hydroxyphenyl)methylene]-5(4H)-oxazolone (Vp), 2-phenyl-4-[(4-methacryloyloxyphenyl)methylene]-5(4H)-oxazalone (VIp) and 2-phenyl-4-[(3-methacryloyloxyphenyl)methylene]-5(4H)-oxazalone have been synthesized for the following investigations.

This paper describes the detailed study of a photochemical reaction where 4-benzyliden-2-phenyloxazolin-5 derivatives take part. We have chosen the oxazalone derivatives as a model object and quantum-chemically modeled their properties. It has been shown that irradiation of 2-phenyl-4-[phenylmethylene]-5(4H)-oxazolone derivatives in various solutions gives a rise to product the *cis* isomerisation. This work was aimed at determining the role of the exited singlet and triplet states in *cis-trans* isomerisation and other photochemical transformation which we have been studied.

2. Experimental part

2. 1. Compounds

Oxazolone derivatives were prepared by condensation

of diferent arylaldehydes with hippuric acid in acetic anhydride, in the presence of anhydrous sodium acetate as a homogeneous basic catalyst, according to the optimized method [28,29].

2-phenyl-4-[[4-acetyloxyphenyl]methylene]-5(4H)-oxazolone (IIIp)

The light yellow crystals were collected by filtration. The product was recrystallized from EtOH, m.p.: 168°C, yield: 80 %.

^{1}H NMR (400 MHz, DMSO-d_6), *%* (ppm): 7.36 (s, 1H, -C**H**=), 2.44 (s, 3H, C**H**$_3$), 8.26-8.18 (m, 4H, Ph-**H**), 7.3-7.65 (m, 5H, Ph-**H**).

UV- VIS (ethanol) λ_{max}: 225, 261, 366 nm.

2-phenyl-4-[[3-acetyloxyphenyl]methylene]-5(4H)-oxazolone (IIIm)

The product was recrystallized from EtOH, m.p. 140^{0}C (lemon coloured crystals from AcOH), yield 75%.

^{1}H NMR (400 MHz, DMSO-d_6), *%* (ppm): 7.32 (s, 1H, -C**H**=), 2.3 (s, 3H, C**H**$_3$), 7.21-8.04 (m, 4H, Ph-**H**), 7.70-8.15 (m, 5H, Ph-**H**).

UV- VIS (ethanol) λ_{max}: 223, 260, 361 nm.

2-(benzoylamino)-3-(4-hydroxyphenyl)-2-propenoic acid (IVp)

IIIp (1 g, 0.003 mol) was dissolved in a solution of AcOH (5 mL) in izopropanol (5 mL) and hydrochloric acid (0.5 mL, 36-38%) was added. The mixture was heated for one hour at 80°C in water bath. The white crystals were collected by precipitation in water. The product was recrystallized from EtOH, m.p.: 210°C, yield: 80 %.

^{1}H NMR (400 MHz, DMSO-d_6), *%* (ppm): 7.35 (s, 1H, -C**H**=), 6.71-8.00 (m, 4H, Ph-**H**), 7.46-7.54 (m, 5H, Ph-**H**), 9.69 (s, 1H, -O**H**), 9.65 (s, 1H, -N**H**).

2-(benzoylamino)-3-(3-hydroxyphenyl)-2-propenoic acid (IVm)

Obtained as described for IVp, m.p. 220°C (white crystals), yield 75%. The product was recrystallized from EtOH.

^{1}H NMR (400 MHz, DMSO-d_6), *%* (ppm): 7.27 (s, 1H, -C**H**=), 6.71-7.572 (m, 4H, Ph-**H**), 7.46-8.00 (m, 5H, Ph-**H**), 9.77 (s, 1H, -O**H**), 9.35 (s, 1H, -N**H**).

2-phenyl-4-[(4-hydroxyphenyl)methylene]-5(4H)-oxazolone (Vp)

(0.8 g, 0.0028 M) IVp was dissolved in DMF (1mL) with phenothiazine inhibitor of radical polymerization. Then the reaction mixture was heated to 75°C during hour. Methacrylic anhydride (2 mL) in DMF (2 mL) was injected gradually to the above solution via a glass syringe while the solution temperature was kept 75°C. The mixer of products Vp and VIp was formed. The yellow crystals Vp were extracted, m.p.: 218°C, yield: 35%.

1H NMR (400 MHz, DMSO-d_6), % (ppm): 7.22 (s, 1H, -C**H**=), 10.27 (s, 1H, -O**H**), 6.88-8.14 (m, 4H, Ph-**H**), 7.60-8.13 (m, 5H, Ph-**H**).

UV- VIS (ethanol) max: 258, 383 nm.

2-phenyl-4-[(4-methacryloyloxyphenyl)methylene]-5(4H)-oxazolone (VIp) was obtained as described for Vp. The resulting precipitate was filtered off, washed with 5% aqueous $NaHCO_3$ and water to neutrality, and finally dried. Purification was performed by recrystallization from hexane. Light yellow crystals; yield 55%; mp 170°C.

^{1}H NMR (400 MHz, DMSO-d_6), *%* (ppm): 5.89 (s, 1H, C**H**$_2$=), 6.34 (s, 1H, C**H**$_2$=), 2.06 (s, 3H, -C**H**$_3$), 7.28-8.18 (m, 4H, Ph-**H**), 7.70-8.35 (m, 5H, Ph-**H**).

2-phenyl-4-[(3-methacryloyloxyphenyl)methylene]-5(4H)-oxazolone (VIm) obtained as described for VIp. Purification was performed by recrystallization from hexane. Light yellow crystals; yield 76%; mp 138°C.

^{1}H NMR (400 MHz, DMSO-d_6), *%* (ppm): 5.90 (s, 1H, C**H**$_2$=), 6.37 (s, 1H, C**H**$_2$=), 2.08 (s, 3H, -C**H**$_3$), 7.25-8.16 (m, 4H, Ph-**H**), 7.67-8.15 (m, 5H, Ph-**H**).

2.2. Methods

^{1}H NMR (400 MHz) spectra was recorded on a "Mercury-400" spectrometer using DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard.

UV-VIS measurements in the 210-600 nm spectral region were performed at room temperature in solutions in quartz cells (C=10^{-5} mol/L) with a Perkin-Elmer UV/VIS/NIR Lambda 19 spectrometer.

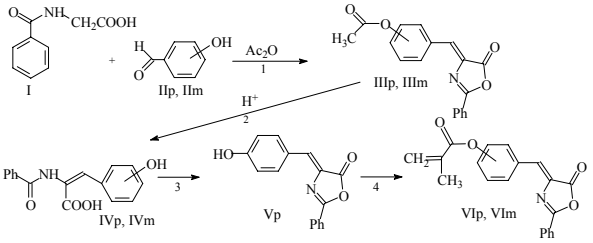
The absorption and steady-state fluorescence spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer and LS-50 Perkin-Elmer spectrofluorometer, respectively. The emission spectra were measured by adjusting the excitation wavelengths to the short-wavelength maximum in the absorption spectra, while fluorescence excitation spectra were recorded at wavelengths corresponding to the maximum in the emission spectra. An intensity scale of fluorescence excitation and fluorescence spectra is given in arbitrary units.

Perkin-Elmer LS fluorescence spectrometer for emission spectra was used. Spectral grade ethyl alcohol and acetonitrile from Fluka were used as solvents in all spectroscopic measurements.

Unconstrained geometry optimizations of molecules in the ground (S_0) and excited singlet (S_1, S_2, S_3, S_4) or triplet (T_1, T_2, T_3) electronic states were carried out using the calculation method of the semi-empirical PM3/CI levels theory [30], with standard procedures being employed together with the EF method [31] implemented in MOPAC program package. On completion of each optimization, the Hessian matrix was calculated and verified for positive definiteness in order to assess whether the structures were truly minimal [32]. The electronic transitions ($S_0 \rightarrow S_n$) were calculated using the ground state geometries. All other transitions ($S_1 \rightarrow S_n$, $S_2 \rightarrow S_n$, $S_3 \rightarrow S_n$, $S_4 \rightarrow S_n$ and $S_n \rightarrow S_0$) were calculated using the excited state geometries. The ground and all excited state configurations, due to excitation within the highest occupied HOMO-1 molecular orbitals as well as the lowest unoccupied LUMO+1 ones, were included in the CI calculations.

3. Results and discussion

By the condensation of hippuric acid I with p- and m-hydrohybenzaldehydes IIp, IIm in acetic anhydride acetylic derivatives IIIm, IIIp have been obtained [28].



Oxazolone cycle opens up with the formation of colorless products IVp and IVm in acidic conditions. The monomers VIp and VIm via acylation of IVp and IVm in metacrylic anhydride were obtained.

Quantum-chemical calculations were carried out for IIIm and 3-vinylphenyl acetate for comparison in order to estimate the photochemical properties of oxazolidones.

To predict the Franck-Condon excitation and emission energies to the various states the ground-state and the excited singlet (S_1, S_2, S_3) or triplet (T_1, T_2, T_3) electronic states, the geometries were optimized and the corresponding Franck-Condon energies were calculated. On the basis of this calculation the diagram with potential energy curves were constructed (Fig.1).

These diagrams showed the potential energy curves of ground and excited singlet or triplet states as well as the possible transitions between them for compounds IIIm and 3-vinylphenyl acetate, as example.

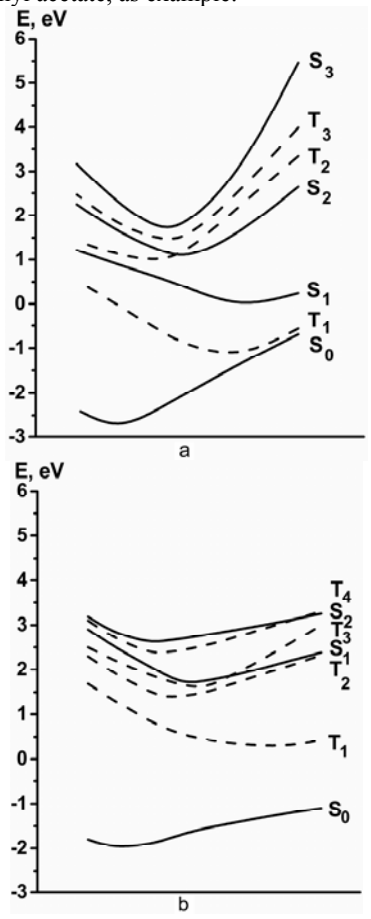


*Fig. 1. Energy diagram for trans- form of IIIm - **a** and for 3-vinylphenyl acetate - **b** according to PM3/CI calculations.*

As we can see, potential curve S_1 is off-centered relative to the potential curve S_0, i.e. transition 0-0 will not be the most intensive in the long-wave length absorption band. The intercombinative transition to the T_1 level is not allowed. Lower level T_1 possesses the $\pi\pi^*$ nature and is not considered as a photoactive one. Both levels may be used for the transmission of cis-trans isomerization, while the S_1 is suitable to fluorescence. The excitation of level S_2 as well as the higher singlet levels may bring to the intercombination conversion S_2- T_2 due to there close location and intersection. Level T_2 possesses the $n\pi^*$ nature being photoactive. The energy diagram for 3-vinylphenyl acetate is included for the comparison.

The changes in electron densities accompanying electronic transitions in cis-2-phenyl-4-[[3-acetyloxyphenyl]methylene]-5(4H)-oxazolone (IIIm) and 3-vinylphenyl acetate were calculated. The results of these calculations are presented in Figure 2. Empty circles indicate the decrease and filled circles the increase of the electron density in the atom, the surface of circles is proportional to the absolute value of the electron density change in the atom.

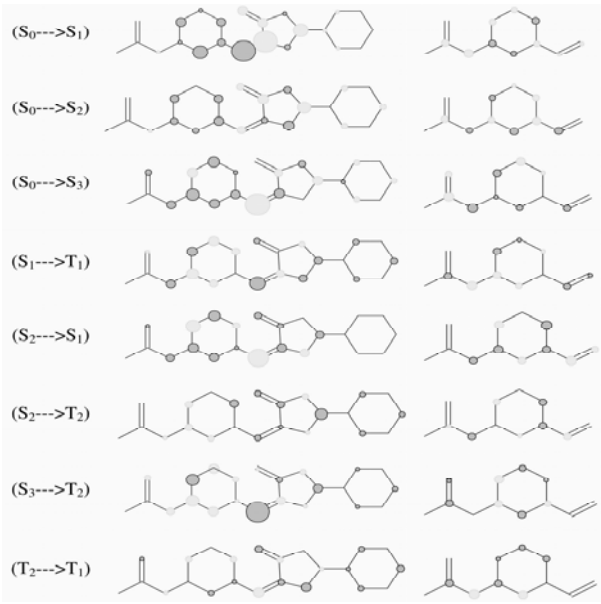


Fig. 2. Calculated changes in electron densities accompanying electronic transitions in cis-2-phenyl-4-[[3-acetyloxyphenyl]methylene]-5(4H)-oxazolone (IIIm) and 3-vinylphenyl acetate.

Fig. 2 shows that electron density remains totally unchanged in any electronic transition with or without multiplicity changing on the carbon of acetyl group. The most changes of the electron density take place on the methenyl group. As a result with any excitation are to take place with no photo-Fries rearrangement products. The calculated values are in a good accordance with experimental ones.

4. Spectral measurements

Investigation of photochemical properties of compounds with oxazolone containing a fragment was conducted taking into account the spectral characteristic which we can study after measurement absorption and fluorescence emission spectra. For the spectral measurements we used acetylic derivatives of oxazolone as modeling compounds of methacrylic monomers. Absorption and fluorescence emission spectra of acetilic derivatives were measured in quartz cells, which were filled with ethanol. The absorption spectra compounds IIIm and IIIp during UV irradiation are represented in Fig. 3.

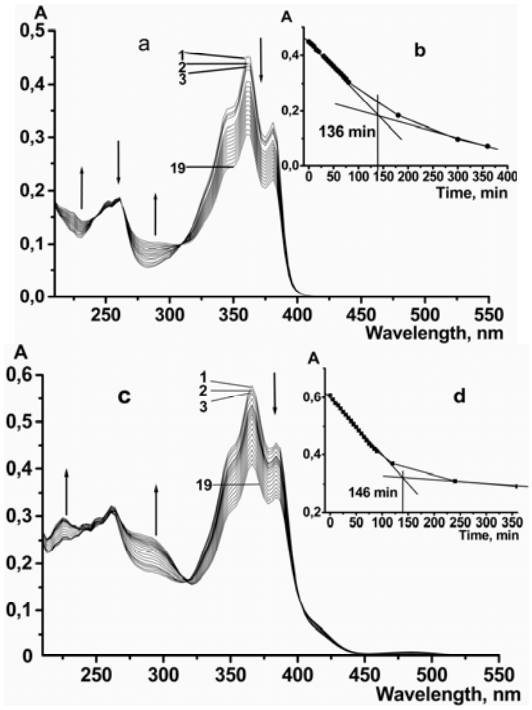


*Fig. 3. Changes in the absorption spectra of IIIm (**a**) and IIIp (**c**) in ethanol (C = 10^{-5} mol/L) before – 1 and after every 5 min periods of irradiation at room temperature; (**b**) and (**d**) - changes of the absorption of solutions on 360 nm during UV- irradiation.*

In the spectrum of absorption the ethanol solutions of products IIIm and IIIp (Fig. 3) have two bands with vibrational structure, i.e. an intensive long-wave band with a molar absorption coefficient on the order 1,35 10^4 M^{-1} cm^{-1} with approximate maximum of 360-365 nm and a medium-intensity absorption band with its maximum about 260 nm (0,52 10^4 M^{-1} cm^{-1}). During the IIIm and IIIp solutions irradiation process the there decolouration is observed accompanied with a drop of the long-wave maximum intensity, as well as an increase of absorption intensity at 360 nm with isosbestic point at 311, 316 nm respectively. The presence of isosbestics points prompting the total invariability of the running processes and absence of the new long-wave maxima of absorption, typical of o-oxyketones structures. The presence of isosbestics points also witnesses no photo-Fries rearrangement.

The solutions decolouration shows the dissolvent joining over the double bond of oxazolone. The half-reaction periods are alike and equal 145 and 146 min., (k=8*10^{-5} c^{-1}) respectively.

In addition the changes of the absorption spectrum IIIm and IIIp in acetonitrile before and after irradiation (Fig. 4) were studied. The similar changes of optical densities were received as in case of use ethanol as solvent.

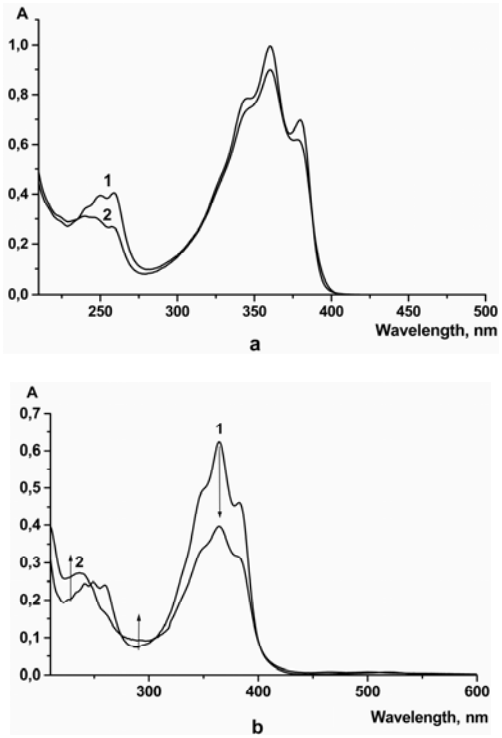


*Fig. 4. Changes in the absorption spectra of IIIm (**a**) and IIIp (**b**) in acetonitrile (C = 10^{-5} mol/L).*

The absorption bands maxima have the same figures within solution spectrums IIIm and IIIp in acetonitrile (Fig. 4), but having the pronounced vibrational structure with 260 nm as well as with 295 nm accordingly.

The irradiation treatment of these compounds in acetonitrile gives only an insignificant decrease of the intensity also brining the smoothing of vibrational structure of the long-wave length absorption band as well as the absorption strength decrease and the redistribution of the vibrational structure intensity in 260 nm. The observable results is typical of the cis-trans isomerization process aryloxazolones [33,34]. Cis-trans isomerization in its pure form is also observed during irradiation in isopropanol (Fig. 5). It has been found out that the half-reaction period in this case equals approximately 20 min., i.e. the reaction constant is 5.77 10-4 c^{-1}. This figure agrees with the one mentioned in [34] for isomerization unsubstituted benzylidenoxazolone in acetonitrile.

The transmission density decrease with 258 nm minus and the displacement of the maximum in the short-wave

area are typical of isomeric form formation [6].

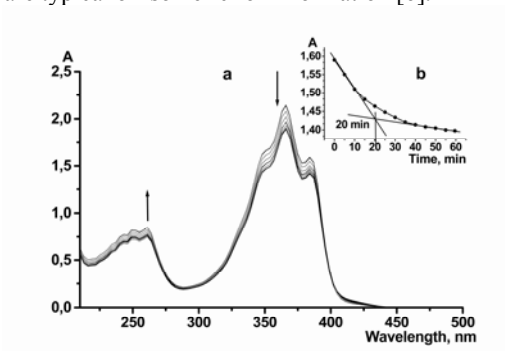


*Fig. 5. Changes in the absorption spectra of IIIp (**a**) in izopropyl alcohol (C = 10^{-5} mol/L) before - 1 and after every 5 min periods of irradiation at room temperature; plots of the differential absorbance changes of irradiated IIIp (**b**) solutions on 360 nm.*

The stable state of the oxazolone molecule is the *cis*-isomeric configuration [35]. The absorption in the visible range of a photon induces the transition to the *trans*-isomer. This state is metastable with the reverse transition to the *cis*- state taking place through photo activation. Therefore, a molecule absorbing of a photon undergoes a complete *cis*-*trans*-*cis* isomerization cycle [36]. From the *trans* form, molecules come back to the *cis* form by two mechanisms – spontaneous thermal reactions and *trans*-*cis* photoisomerization.

The normalised absorption, fluorescence of excitation and fluorescence spectra of IIIm and IIIp in acetonitrile are shown in Fig.6.

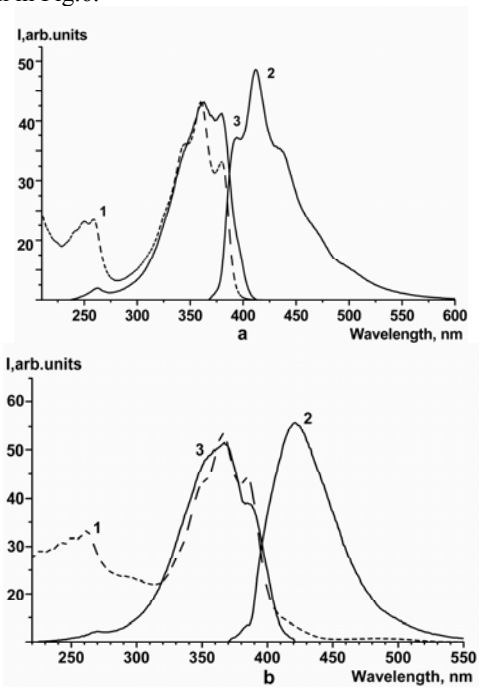


*Fig. 6. The absorption -1, emission (λ_{ex}=350 nm) -2, fluorescence of excitation (λ_{abs}=420 nm) -3 of IIIm (**a**) IIIp (**b**) in acetonitrile at room temperature.*

The emission was observed between 370 and 600 nm with λ_F at 419 nm for IIIp and 412 nm for IIIm, corresponding to $S_1 \rightarrow S_0$ transition.

In the excitation spectra of the IIIm and IIIp fluorescence the second transmission (within the 260 nm area) is practically absent, which proves the fluorescence reaction to be possible only by excitation in the S_1 level.

The fluorescence quantum yields were determined by a comparative method with a reference standard of anthracene (ethanol, excitation 366 nm, φ_f 0.27) [37]. All the solutions, including that of anthracene, were excited at 350 nm in the wavelength region of 355–730 nm. It was found that fluorescence quantum yield of IIIm and IIIp in ethanol are $2{,}4*10^{-3}$, $1*10^{-3}$ respectively.

The methacrylic monomers based on oxazolone derivatives offer great promise for practical device applications due to their photochemical properties particularly for reversible optical data storage.

5. Conclusions

The present work reflects the theoretical and experimental investigations of the photochemical properties of the oxazalone derivatives. The idea of the photo-Fries reaction impossibility by UV-irradiation has been obtained with the help of quantum chemical calculations.

The calculated values were confirmed by spectral measurements. The total understanding of the relationship between the structure and photochemical properties of oxazalone derivatives reveals the possibility for their potential applications in the field of photonics and optoelectronics. Polymers based on them are very promising for reversible optical data storage as well as the orientation of photochromic polymers, the photoalignment of liquid crystals and all-optical processing.

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References

[1] K. Khan, U. Mughal, M. Khan, Z. Ullah, S. Perveenb, M. Choudhary, Bioorg. Med. Chem. **14**, 6027 (2006).
[2] M. A. Mesaik, S. Rahat, K. M. Khan, M. I. Choudhary, M. Shahnaz, Z. Ismaeil, Bioorg. Med. Chem. **12,** 2049 (2004).
[3] K. Roy, S. Chakraborty, A. Sahab, Bioorg. Med. Chem. Lett. **13**, 3753 (2003)–3757.
[4] H. Joshi, P. Upadhyay, D. Karia, A. Baxi, European Journal of Medicinal Chem. **38**, 837 (2003).
[5] C. Cativiela, J. M. Fraile, J. J. Garcia, M. P. Lopez, J. A. Mayoral, E. Pires, Tetrahedron: Asymmetry **7**, 2391 (1996).

[6] A. Fernandez-Gonzalez, R. Badia, M.E. Diaz-Garcia, Anal. Biochem. **341**, 113 (2005).
[7] G. Koczan, G. Csik, A. Csampai, E. Balog, S. Bosze, P. Sohar, F. Hudecz, Tetrahedron. **57**, 4589 (2001).
[8] S. Icli, H. Icli, H. Koc, A. McKillop, Spectrosc. Lett. **27,** 1115 (1994).
[9] S. Icli, A. O. Doroshenko, S. Alp, N. A. Abmanova, S. I. Egorova, S. T. Astley, Spectrosc. Lett. **32**, 553 (1999).
[10] E. Erlenmeyer, J. Anal. Chem. **1**, 275 (1893).
[11] K. Gottwald, D. Seebach, Tetrahedron. **55**, 723 (1999).
[12] J. Meiwes, M. Schudock, G. Kretzschmar, Tetrahedron: Asymmetry. **8**, 527 (1997).
[13] D. Seebach, G. Jaeschke, K. Gottwald, K. Matsuda, R. Formisano, D.A. Chaplin, Tetrahedron. **53**, 7539 (1997).
[14] N. W. Boaz, S. D. Debenham, S. E. Large, M. K. Moore, Tetrahedron: Asymmetry. **14**, 3575 (2003).
[15] P. Wipf, C.P. Miller, J. Org. Chem. **58**, 3604 (1993).
[16] C. J. Moody, K. J. Doyle, Progress in Heterocyclic Chemistry, (Eds.: G. W. Gribble, T. L. Gilchrist), Pergamon, Oxford, U.K, 1997.
[17] P. Wipf, L.T. Rahman, S.R. Rector, J. Org. Chem. **63**, 7132 (1998).
[18] G. Ozturk, S. Alp, K. Ertekin, Dyes and Pigments. **72**, 150 (2007).
[19] K. Ertekin, S. Alp, C. Karapire, B. Yenigul, E. Henden, S. Icli, J. Photochem. Photobiol. A. **137**, 155 (2000).
[20] H. Kobsa, J.Org. Chem. **27**, 2293 (1962).
[21] J. C. Anderson, C. B. Reese, J. Chem. Soc. **63**, 1781 (1963).
[22] O. L. Chapman. Organic Photochemistry.,Marcel. Dekker Inc., New. York, 1967.
[23] D. Bellus, Adv. Photochem. **8**, 109 (1971).
[24] D. P. Kelley, J.T. Pinkey, Tetrahedron Lett. **5**, 3427 (1964).
[25] H. Shizuka, Bull. Chem. Soc. Japn. **42**, 52 (1969).
[26] R.A. Finnegan, J.J. Mattice, Tetrahedron. **21**, 1015 (1965).
[27] H. Obara, H. Takahashi, H. Hirano, Bull. Chem. Soc. Japn. **42**, 560 (1969).
[28] S. K. Li, J. E. Guillet, Macromolecules. **10**, 840 (1977).
[29] C. Yu, B. Zhou, W. Su, Z. Xu, Synthetic Comm. **36**, 3447 (2006).
[30] J. J. P. Stewart, J. Comput. Chem. **10,** 209 (1989).
[31] J. Baker, P.M.W. Gill, J. Comput. Chem. **9**, 465 (1988).
[32] J. J. P. Stewart, J. Comput. Auded Mol. Des. **4**, 1 (1990).
[33] E. F Ullman, N. Baumann, J. Am. Chem. SOC. **192,** 5892 (1970).
[34] K. Brocklehurst, K. Williamson, Tetrahedron. **30**, 351 (1974).
[35] N. Baumann, E.F. Ullman, J. Am. Chem. SOC. **90**, 4158 (1968).
[36] Y. S. Rao, J. Org. Chem. **41**, 722 (1976).
[37] W. H. Melhuish, J. Phys. Chem. **65**, 229 (1961).

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