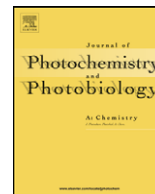




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Spectroscopy and photophysics of dimethyl-substituted alloxazines

Marek Sikorski^{a,*}, Dorota Prukała^a, Małgorzata Insińska-Rak^a, Igor Khmelinskii^b,
David R. Worrall^c, Sian L. Williams^c, Jordi Hernando^d, Jose L. Bourdelande^d,
Jacek Koput^a, Ewa Sikorska^e

^a Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

^b Universidade do Algarve, FCT, Campus de Gambelas, 8005-139 Faro, Portugal

^c Department of Chemistry, Loughborough University, Leicestershire LE11 3TU, UK

^d Unitat de Química Orgànica, Universitat Autònoma de Barcelona, Bellaterra, Barcelona 08193, Spain

^e Faculty of Commodity Science, The Poznań University of Economics, al. Niepodległości 10, 60-967 Poznań, Poland

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ABSTRACT

We have calculated the electronic structure and absorption spectra from the ground state and the first triplet excited state for five dimethylalloxazines, using the TD-DFT approach. The results of the calculations were correlated to experimental spectral and photophysical data, including the transient spectra reported here containing triplet–triplet absorption data, using the proximity effect theory to explain the variations of the ISC rates with the substitution pattern and solvent. Additionally, singlet oxygen yields were measured for these compounds, demonstrating their high efficiency as singlet oxygen photosensitizers.

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1. Introduction

The term ‘flavins’ refers to the 10-substituted 7,8-dimethyl-2,3,4,10-tetrahydro-benzo[g]pteridine-2,4-diones, lumiflavin (7,8,10-trimethyl-10H-benzo[g]pteridine-2,4-dione) being the parent molecule from which all other variants derive, e.g., vitamin B₂ (riboflavin), flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD). The motivation behind the large effort put into flavin studies over a number of years comes from the realization that the excited states of flavins play an important role in living organisms and are involved in a number of important photobiological and photochemical processes, such as phototropism, phototaxis, and photodynamic action. The photochemistry of isoalloxazines (10-substituted 2,3,4,10-tetrahydro-benzo[g]pteridine-2,4-diones), and especially the photochemistry of flavins (7,8-dimethyl-substituted isoalloxazines) has been the subject of intense research over the years [1].

In contrast to flavins, the closely related alloxazines (benzo[g]pteridine-2,4(1H,3H)-diones) have received relatively little attention. The major aspects of the spectroscopy of alloxazines in their singlet states are understood fairly well, but, with the exception of our own recent studies [2–6], the published data were mostly limited to steady-state measurements of absorption and fluorescence [7]. The early interest in the spectral and photophysical properties of alloxazines, including lumichrome (7,8-dimethylalloxazine = 7,8-dimethylbenzo[g]pteridine-2,4(1H,3H)-dione), was driven mainly by their similarity to isoalloxazines and in particular to flavins. They were also the subject of interest as photodecomposition products of flavins. Some of the interest in alloxazines has been driven by the discovery of excited-state double proton transfer (ESDPT) in lumichrome in the presence of acetic acid [8,9]. Alloxazines and related compounds belong to an interesting group of species whose hydrogen-bonded complexes are capable of undergoing ESDPT; we have examined the mechanism of photo-initiated double proton transfer for a set of differently substituted methyl- and cyanoalloxazines in 1,2-dichloroethane [10]. In a more detailed recent study, we have investigated the photoinduced proton transfer of lumichrome in the presence of acetic acid in 1,2-dichloroethane, acetonitrile and pure acetic acid [11–14]. Presently, the interest in

* Corresponding author. Tel.: +48 61 8291309; fax: +48 61 8658008.
E-mail address: sikorski@amu.edu.pl (M. Sikorski).

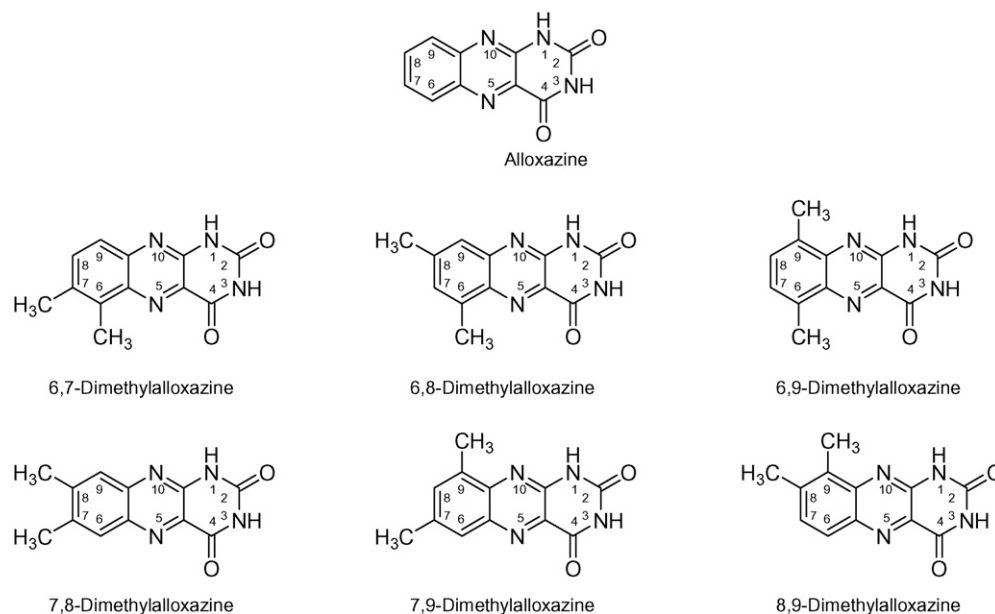


Fig. 1. Structure of alloxazines and their atom numbering.

alloxazines is a focal point of a growing body of research, motivated by remarkable new findings, and discoveries of promising practical applications of alloxazines, described below.

To give some examples of the important findings of recent years, we shall note that lumichrome has been identified as the first natural metamorphosis-inducing substance in ascidians [15,16]. In contrast, riboflavin, a possible parent compound of lumichrome, has been found inactive in induction of larval metamorphosis. It has been shown that *Sinorhizobium meliloti* bacteria produce lumichrome that enhances root respiration in alfalfa (*Medicago sativa* L.) and also triggers a compensatory increase in whole-plant net carbon assimilation [17]. The well-known rapid degradation of riboflavin to lumichrome under many physiological conditions and the prevalence of riboflavin release by rhizosphere bacteria suggest

that the events demonstrated in the *S. meliloti*-alfalfa association may be widely important across many plant-microbe interactions.

Some other interesting facts, which have increased the recent interest in alloxazines, include an important conclusion of our studies that alloxazines and lumichromes are efficient singlet oxygen photosensitizers [18–20]. Alloxazine nucleosides are potentially of interest as fluorescent probes and have been predicted to exhibit hydrogen-bonding characteristics similar to those of thymidine [21]. Recently, it has been proposed that alloxazines may play an important role in the photodegradation of polyamidehydroxyurethane polymers in aqueous solution, and that singlet oxygen may be involved in the process [22]. High-quality alloxazine-imprinted polymers have been prepared and proposed for application in HPLC analysis [23]. Remarkably, strong binding

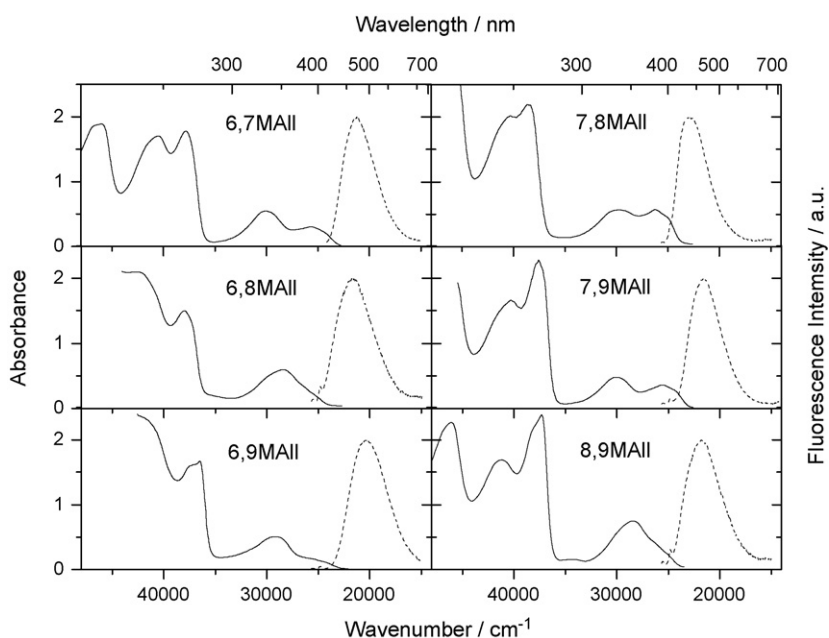


Fig. 2. Absorption (solid line) and fluorescence (dashed line) spectra of dimethylalloxazines in acetonitrile solutions.

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