Journal of Photochemistry and Photobiology A: Chemistry 199 (2008) 345–352

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photosensitized generation of singlet molecular oxygen by aryloxazinones

Else Lemp[a,1], Alvaro Cañete[a,1], German Günther[a,1], Nancy Pizarro[b], Antonio L. Zanocco[a,*]

[a] Universidad de Chile, Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química Orgánica y Fisicoquímica, Casilla 233, Santiago - 1, Santiago, Chile
[b] Universidad Andrés Bello, Facultad de Ecología y Recursos Naturales, Departamento de Ciencias Químicas, República 275, Santiago, Chile

ARTICLE INFO

Article history:
Received 8 April 2008
Received in revised form 16 June 2008
Accepted 18 June 2008
Available online 27 June 2008

Keywords:
Singlet molecular oxygen
Aryloxazinones
Photosensitization
Photophysics
Photostability

ABSTRACT

The photophysical properties, the capacity to produce singlet molecular oxygen by sensitization and the photostability of a series of 20 aryloxazinones and one quinoxalinone have been evaluated using a combination of methods including steady-state and time-resolved spectroscopic techniques. The photophysics of aryloxazinone derivatives and consequently its capacity to produce singlet molecular oxygen is very dependent on the structure. Benzoxazinone derivatives substituted in para position to the 2-phenyl group (**1**)–(**3**) have low fluorescence quantum yields and produce singlet oxygen in moderate quantum yields. Inclusion of electron donors groups in position 7 of the aromatic fused moiety to the heterocyclic ring (**4**)–(**6**), increases significantly the emission from the excited singlet state with a concomitant diminution in the ability to produce singlet oxygen. An exception corresponds to the 7-methoxy-2-phenylbenzoxazinone (**4**) able to generate larger quantities of excited oxygen and photodecompose in less than a 2% under large energy doses in aerobic irradiation conditions. In general, 2-phenyl and 2-methyl naphthoxazinones derivatives (**7**)–(**17**) are more fluorescent than the compounds of the corresponding benzo series, and generate singlet molecular oxygen in low to moderate yields. Exceptions are the 2-methyl (**13**) and the 9-methoxy-2-methyl (**14**) derivatives that produce excited oxygen efficiently, however, with appreciable decomposition. The most promising compounds to be employed as singlet oxygen sensitizers are the anthracene like 3-phenyl-2H-naphtho[2,3-b][1,4]-oxazin-2-one (**19**) and the 1-methyl-3-phenylquinoxalin-2(1H)-one (**21**). These compounds are photostable in the absence and in the presence of electron donor additives under large doses of irradiation, accomplishing all requisites to be good sensitizer and to produce singlet oxygen in high yields, almost independently on solvent polarity.

1. Introduction

At present, photosensitization is the most utilized method to produce singlet molecular oxygen, $O_2(^1\Delta_g)$, in solution [1–3]. Photosensitized generation is a simple and controllable method for the production of $O_2(^1\Delta_g)$, requiring only oxygen, light of an appropriate wavelength, and a photosensitizer capable of absorb and use the energy to promote oxygen to its singlet excited state. There are two described mechanisms, Types I and II, and most of photosensitizers react through one of them or both simultaneously. Type I mechanism involves hydrogen-atom abstraction or electron-transfer between the excited sensitizer and a substrate, yielding free radicals. These radicals can react with oxygen to form an active oxygen species such as the superoxide radical anion. In Type II mechanism, singlet oxygen is generated via an energy transfer process during a collision of the excited sensitizer with triplet oxygen. During last years, a new proposal using a third-order nonlinear-optical process that consists in simultaneous absorption of two photons to excite the sensitizer has been employed [3,4]. Two-photon excitation of several photosensitizers to produce singlet oxygen in different experimental conditions and its eventual application in photodynamic therapy has been deeply and extensively studied by Ogilby and coworkers [5–10]. So the excitation wavelength is twice of the actual transition wavelength, allowing the use of near-IR photons corresponding to the tissue transparency window. Furthermore, this technique does not require the use of sensitizers with red shifted lowest absorption band. Despite the excitation method, each photosensitizer molecule can typically produce 10^3–10^5 molecules of $O_2(^1\Delta_g)$ before being degraded through photobleaching mainly by Type I process and/or by reaction with previouly produced $O_2(^1\Delta_g)$. The corresponding quantum yield of singlet molecular oxygen, Φ_Δ, depends on the O_2 concentration and on the nature of the solvent for compounds which sensitize $O_2(^1\Delta_g)$ via quenching of their lowest singlet (S_1) and or triplet (T_1) excited state by oxygen ground state. However, Φ_Δ does

* Corresponding author. Tel.: +56 2 9782877; fax: +56 2 9782868.
E-mail address: azanocco@ciq.uchile.cl (A.L. Zanocco).
[1] Tel.: +56 2 9782877; fax: +56 2 9782868.

1010-6030/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2008.06.014

not depend on the oxygen concentration at $[O_2] \geq 2 \times 10^{-4}$ M, for compounds without $[O_2]$-dependent intersystem-crossing quantum yield. There are several groups of UV–vis absorbing molecules that have shown singlet oxygen generating ability. Photosensitizers should exhibit the following properties: (1) high molar absorption coefficient in the spectral region of the excitation light; (2) a triplet state of appropriate energy ($E_T \geq 95$ kJ mol^{-1}) to allow efficient energy transfer to ground state oxygen; (3) high quantum yield of the triplet state ($\Phi_T > 0.4$) and long triplet state lifetimes ($\tau_T > 1$ μs), since the efficiency of the photosensitizer is dependent on the photophysical properties of its lowest excited triplet state; and finally (4) high photostability. The majority of photosensitizers are organic molecules including several families of compounds and probably the most popular are phenothiazinium derivatives [1,11], xanthene dyes [1,12,13], aromatic hydrocarbons such as napthalenes, anthracenes, biphenyls, dibenzanthracene, pyrene, fluoranthene, 1,11-benzoperlyene and perlyene [1,14–16], quinone and anthraquinone derivatives [17–20], aromatic ketones [1,21,22] porphyrins derivatives [23,24], phthalocyanines [25,26], naphthalocyanines [27,28] chlorins and bacteriochlorins [29–32]. Several of these families include heterocyclic rings in their structure. Aryloxazinone-derivatives are a class of heterocyclic compounds that exhibit interesting spectral and photophysical properties such as broad first absorption band, emission in the red, intense fluorescence in both organic solutions and crystalline state, large dipole moment increasing in the excited state, large Stokes shift, and short fluorescence lifetimes [33–36]. In addition, several of these compounds are fairly photostable in the absence of additives, yielding a single photoproduct arising from the triplet state. In the presence of electron donors such as amines, the photoconsumption quantum yield increases and the product distribution changes, the primary photoproduct being a dihydro-naphthoxazinone that photoreacts further yielding ultimately an oxazoline derivative. However, even in the presence of amines, photoconsumption quantum yields are smaller than 0.02. Regarding these properties, it has been suggested that these type of compounds can be employed as quantum counters, wavelength shifters, fluorescent solar concentrators, fluorescent probes for biological systems, and laser dyes [37–45]. Last years, we are interested in studying the dependence of photophysical and phochemical properties of naphthoxazinone derivatives and related compounds on the structure. Our aim it is to introduce structural modifications and/or include substituents (mainly electron donors) to increase the ground/excited dipolar moment shifting the absorption/emission spectra towards longer wavelenghts. Also, we note that studies addressing the evaluation of the ability of aryloxazinones to produce singlet molecular oxygen by photosensitization have not been carried out. Considering the fact that for these compounds, and in general, the intersystem-crossing process is highly dependent on the molecular structure, we expect differences on the triplet yield and therefore on the singlet oxygen quantum yield when an oxazinone ring is condensed to the benzene or the naphthalene rings with different substituents. In this work, we report on sensitized singlet oxygen production by a series of aryl-oxazinone derivatives including several substituent groups in their structures (Fig. 1). Some of these compounds contain a phenyl group at the α-carbonyl position, which should prevent the formation of cyclic photoproducts [46,47]. In addition, when the aryl moiety corresponds to a naphthalene, they differ in the position where the oxazinone ring is fused to the aryl group and in their relative orientation. These differences result in significant changes in their photophysical properties. In addition, we evaluate the substrate photostability under large energy doses of pulsed laser. The properties evaluated for these compounds suggest that some of them are valuable candidates to be employed as singlet oxygen sensitizers in several solvents.

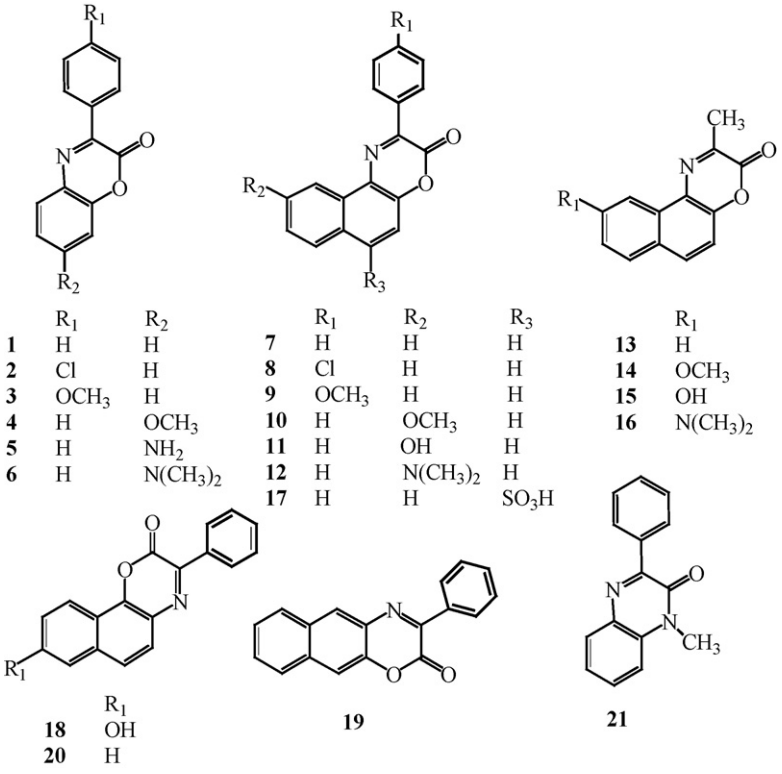

Fig. 1. Chemical structures of the studied compounds.

2. Experimental

2.1. General

All solvents used in syntheses, spectroscopic and kinetic measurements were reagent grade, spectroscopic or HPLC quality, and were purified by the usual procedures when necessary. NMR spectra were recorded employing Bruker DRX-300 spectrometer. Chemical shifts are referred to the internal standard tetramethylsilane, TMS. Elemental analyses were obtained in a Fisons EA – 1108 instrument. IR spectra were recorded using a FT Bruker IFS-56 spectrometer. UV–visible measurements were made in a Unicam UV-4 spectrophotometer. A Fisons MD-800 GC–MS system with a Hewlett Packard Ultra-2 capillary column (25 m) was used to obtain electron impact mass spectra. Steady-state fluorescence spectra were recorded in a Fluorolog Tau-2 spectrofluorometer (SPEX, Jobin Ybon). Phosphorescence spectra were recorded at 77 K in a Fluoromax 2 spectrofluorometer (SPEX, Jobin Ybon) equipped with low-temperature sample-holder accessory. In all other cases, spectroscopic measurements were performed at room temperature. Triplet lifetimes were measured by using a home-made nanosecond laser flash photolysis apparatus equipped with a Quantel Brilliant Q-switched Nd-YAG laser (355 nm, 5 ns pulsewidth, 1–10 mJ per pulse) for excitation. The time profile of the triplet absorption was monitored at 90° by a white-light beam produced by a Xe lamp, and the light transmitted by the sample was spectrally resolved using a monochromator and detected with a photomultiplier. Its output was fed into a digital oscilloscope through a 50 Ohm resistor. Typically 10 shots were averaged to improve the signal-to-noise ratio. Time-resolved singlet oxygen phosphorescence detection, TRPD, at 1270 nm was carried out in 0.5 cm fluorescence cells at 20 °C. Samples were excited by the second harmonic (355 nm, ca. 3–6 mJ per pulse) of a 6-ns light pulse of a Quantel Brilliant Q-Switched Nd:YAG laser. A liquid-nitrogen cooled North Coast model EO-817P germanium photodiode detector with a built-in preamplifier was used to detect infrared radiation from the cell. The detector was at a right-angle to the cell. An interference filter (1270 nm, Spectrogon US, Inc.) and a cut-off filter (995 nm, Andover Corp.) were the only elements between the cell face and the diode cover plate. The preamplifier output was fed into the 1 MΩ input of a digitizing oscilloscope Hewlett Packard model 54540 A. Computerized experiment control, data acquisition and analysis were performed with LabView based software developed in our laboratory. The fluorescence quantum yields (Φ_F) were measured by the comparative method described by Eaton [48] and Demas and Crosby [49], using quinine sulphate in 0.1N sulfuric acid ($\Phi_F = 0.55$) or fluorescein in 0.1 N NaOH ($\Phi_F = 0.92$) as references [50]. The efficiencies of intersystem crossing were determined by observing the 1,3-pentadiene photoisomerization sensitized by benzophenone [51]. Optical densities of sample and reference solutions were set below 0.2 at the excitation wavelength and the fluorescence spectra were corrected by using Rhodamine G as reference. Fluorescence lifetimes, τ_S^0, were measured by employing the phase demodulation method using fluorescein as reference ($\tau_S^0 = 4.05$ ns) [52,53]. Geometry optimizations and Franck-Condon transitions calculations were carried out with Gaussian 03 W, version 6.1, installed in a PC equipped with an Intel Core 2 Quad Q6600 and 4 Gb of RAM memory.

2.2. Chemical synthesis

Naphthoxazinones-derivatives were obtained by employing previously described methods [33,54–56]. A typical procedure is described for benzoxazinone (**1**).

2.2.1. 3-Phenyl-2H-benzo[b][1,4]-oxazin-2-one (*1*)

Freshly distilled methyl benzoylformiate (3.51 mmol) and 2-aminophenol (3.66 mmol) in 25 mL of ethanol were heated at 110 °C by 1 h in a flask equipped with a reflux condenser and a magnetic stirrer. The precipitate obtained by cooling the mixture in ice-water bath was filtered and washed at least three times with each: water, diluted HCl and water. Finally, the dry solid was recrystallized from acetonitrile to yield 0.69 g (85%) of the product as a white crystalline solid. ^{1}H NMR ($CDCl_3$): 8.34 [dd, J = 7.02 Hz, J = 2.09 Hz, 2H]; 7.85 [dd, J = 7.90 Hz, J = 1.55 Hz, 1H]; 7.52 [m, 4H]; 7.39 [d, J = 7.70 Hz, 1H]; 7.33 [dd, J = 8.17 Hz, J = 1.25 Hz, 1H]. ^{13}C NMR ($CDCl_3$): 160.4; 152.3; 150.9; 146.5; 134.1; 131.7; 131.4^d; 131.1; 129.4; 128.4^d; 125.8; 116.2. IR (KBr) cm^{-1}: 1747.6 (C=O), 1605 (C=N). Elem. anal.: cal. %C = 75.33; %H = 4.06; %N = 6.27; exp. %C = 74.98; %H = 4.15; %N = 6.33.

2.2.2. 3-p-Chlorophenyl-2H-benzo[b][1,4]-oxazin-2-one (*2*)

^{1}H NMR ($CDCl_3$): δ 8.34 [dd, J = 6.81 Hz, J = 1.98 Hz, 2H]; 7.84 [dd, J = 7.92 Hz, J = 1.54 Hz, 1H]; 7.53 [t, J = 4.80 Hz, 1H]; 7.46 [dd, J = 6.82 Hz, J = 2.00 Hz, 2H]; 7,40 [t, J = 4.81 Hz, 1H]; 7.30 [t, J = 8.19 Hz, 1H]. ^{13}C NMR ($CDCl_3$): δ 152.6; 149.4; 146.8; 138.2; 132.8; 131.905; 131.8; 131.2^d; 129.9; 129.1^d: 126.1; 116.6. IR (KBr) cm^{-1}: 1732.7 (C=O), 1605.1 (C=N), 695 (C–Cl). Elem. anal.: cal. %C = 65.26; %H = 3.13; %N = 5.44; exp. %C = 64.70; %H = 3.27; %N = 5.45.

2.2.3. 3-p-Methoxyphenyl-2H-benzo[b][1,4]-oxazin-2-one (*3*)

^{1}H NMR ($CDCl_3$): δ 3.89 [s, 3H]; 8.40 [dd, J = 8.84 Hz, J = 2.04 Hz, 2H]; 7.82 [dd, J = 8.84 Hz, J = 1.6 Hz, 1H]; 7.48 [t, J = 9.35 Hz, 1H]; 7.33 [m, 2H]; 7.01 [dd, J = 9.98 Hz, J = 2.04 Hz, 2H]. ^{13}C NMR ($CDCl_3$): δ 162.7; 152.9; 158.3; 146.6; 132.1^d; 131.8; 130.9; 129.5; 127.2; 125.9; 116.5; 114.2^d; 55.9. IR (KBr) cm^{-1}: 1733.4 (C=O), 1607.3 (C=N), 1258.2 (O–C). Elem. anal.: cal. %C = 71.44; %H = 4.38; %N = 5.53; exp. %C = 70.98; %H = 4.51; %N = 5.59.

2.2.4. 3-Phenyl-7-methoxy-2H-benzo[b][1,4]-oxazin-2-one (*4*)

^{1}H NMR ($CDCl_3$): δ 3.41 [s, 3H]; 6.88 [d, J = 2.65 Hz,1H]; 6.95 [dd, 1H]; 7.49 [m, 3H]; 7.75 [d, J = 8.8 Hz, 1H]; 8.29 [m, 2H]. ^{13}C NMR ($CDCl_3$): δ 55.9; 99.9; 113.3; 126.2; 128.3^d; 129.0^d; 130.3; 130.8; 134.3; 147.1; 148.0; 152.5; 162.0. IR (KBr) cm^{-1}: 1739.1 (C=O), 1608.4 (C=N), 1271.7 (O–C). Elem. anal.: cal. %C = 71.14; %H = 4.38; %N = 5.53; exp. %C = 70.82; %H = 4.43; %N = 6.01.

2.2.5. 3-Phenyl-7-amino-2H-benzo[b][1,4]-oxazin-2-one (*5*)

^{1}H NMR ($CDCl_3$): δ 5.96 [s, 2H]; 6.05 [d, J = 2.29 Hz, 1H]; 6.68 [dd, J = 2.32 Hz, J = 8.70 Hz, 1H]; 7.44 [m, 4H]; 8.19 [m, 2H]. ^{13}C NMR ($CDCl_3$): δ 153.6; 153.3; 149.5; 135.7; 130.8; 130.1; 128.9^d; 128.5^d; 124.0; 113.3; 98.8. IR (KBr) cm^{-1}: 1713.9 (C=O), 1617.6 (C=N), 1558.2 (N–H).

2.2.6. 3-Phenyl-7-N,N-dimethylamino-2H-benzo[b][1,4]-oxazin-2-one (*6*)

^{1}H NMR ($CDCl_3$): δ 3.1 [s, 6H]; 6.46 [d, J = 2.71 Hz, 1H]; 6.70 [dd, 1H]; 7.49 [m, 3H]; 7.60 [d, J = 9.03 Hz, 1H]; 8.29 [m, 2H]. ^{13}C NMR ($CDCl_3$): δ 40.3; 96.9; 110.0; 123.5; 128.2^d; 128.6^d; 129.9; 130.1; 135.1; 143.4; 148.8; 152.3; 153.4. IR (KBr) cm^{-1}: 1722.2 (C=O), 1612.9 (C=N). Elem. anal.: cal. %C = 72.16; %H = 5.30; %N = 10.52; exp. %C = 72.06; %H = 5.38; %N = 10.92.

2.2.7. 2-Phenyl-3H-naphtho[2,1-b][1,4]-oxazin-3-one (*7*)

^{1}H NMR ($CDCl_3$): δ 7.37 [d, J = 9.0 Hz, 1H]; 7.49 [m, 3H]; 7.53 [dd, 1H]; 7.65 [dd, 1H]; 7.83 [d, J = 8.1 1H]; 7.90 [d, J = 9.0 Hz, 1H]; 8.46 [m, 2H]; 8.84 [d, J = 8.35 Hz, 1H]. ^{13}C NMR ($CDCl_3$): δ 116.1; 123.3; 126.8; 127.1; 128.5; 128.7; 128.8^d; 129.9^d; 130.9; 131.5; 131.7; 132.8; 134.9; 145.2; 148.8. IR (KBr) cm^{-1}: 1725.7 (C=O),

1584.9 (C=N). Elem. anal.: cal. %C = 79.11; %H = 4.06; %N = 5.13; exp. C% = 79.11; %H = 4.08; %N = 5.93.

*2.2.8. 2-p-Chlorophenyl-3H-naphtho[2,1-b][1,4]-oxazin-3-one (**8**)*

^{1}H NMR ($CDCl_3$): δ 7.40 [m, 3H]; 7.55 [t, *J* = 15.30 Hz, 1H]; 7.68 [t, *J* = 15.30 Hz, 1H]; 7.83 [d, *J* = 8.10 Hz, 1H]; 7.92 [d, *J* = 8.99 Hz, 1H]; 8.46 [dd, *J* = 6.80 Hz, *J* = 2.44 Hz, 2H]; 8.82 [d, *J* = 8.36 Hz, 1H]. ^{13}C NMR ($CDCl_3$): δ 116.1; 123.3; 126.8; 127.1; 128.5; 128.7; 128.8[d]; 129.9[d]; 130.9; 131.5; 131.7; 132.8; 134.9; 145.2; 148.8. IR (KBr) cm^{-1}: 1722.6 (C=O), 1589.6 (C=N). Elem. anal.: cal. %C = 70.25; %H = 3.28; %N = 4.55; exp. %C = 70.25; %H = 3.34; %N = 4.65.

*2.2.9. 2-p-Methoxiphenyl-3H-naphtho[2,1-b][1,4]-oxazin-3-one (**9**)*

^{1}H NMR ($CDCl_3$): δ7.39 [m, 3H]; 7.51 [t, *J* = 15.30 Hz, 1H]; 7.66 [t, *J* = 15.30 Hz, 1H]; 7.79 [d, *J* = 8.10 Hz, 1H]; 7.93 [d, *J* = 8.96 Hz, 1H]; 8.51 [dd, *J* = 6.80 Hz, *J* = 2.44 Hz, 2H]; 8.88 [d, *J* = 8.36 Hz, 1H]; 3.90 [s, 3H]. ^{13}C NMR ($CDCl_3$): δ 55.6; 114.1; 122.5; 126.1; 127.1; 128.1; 127.9; 128.8[d]; 130.0[d]; 130.9; 131.5; 131.7; 132.8; 135.0; 146.2; 152.8. IR (KBr) cm^{-1}: 1723.6 (C=O), 1632.1 (C=N), 1256.0 (O–C). Elem. anal.: cal. %C = 75.24; %H = 4.32; %N = 4.62; exp. %C = 74.46; %H = 4.33; %N = 4.64.

*2.2.10. 2-Phenyl-9-methoxy-3H-naphtho[2,1-b][1,4]-oxazin-3-one (**10**)*

^{1}H NMR ($CDCl_3$): δ 4.01 [s, 3H]; 7.23 [dd, 1H]; 7.29 [d, *J* = 9.48 Hz, 1H]; 7.57 [m, 3H]; 7.79 [d, *J* = 8.92 Hz, 1H]; 7.90 [d, *J* = 8.89 Hz, 1H]; 8.22 [d, *J* = 2.43 Hz, 1H]; 8.51 [m, 2H]. ^{13}C NMR ($CDCl_3$): δ 55.6; 101.6; 112.8; 118.8; 125.7; 126.2; 128.4[d]; 129.3[d]; 129.7; 131.1; 132.1; 132.3; 134.6; 145.5; 152.9; 155.0; 159.8. IR (KBr) cm^{-1}: 1732.3 (C=O), 1623.7 (C=N), 1242.3 (O–C). Elem. anal.: cal. %C = 75.24; %H = 4.32; %N = 4.62; exp. %C = 75.19; %H = 4.58; %N = 4.62.

*2.2.11. 2-Phenyl-9-hydroxy-3H-naphtho[2,1-b][1,4]-oxazin-3-one (**11**)*

^{1}H NMR ($CDCl_3$): δ 5.37 [s, 1H]; 7.23 [dd, 1H]; 7.31 [d, *J* = 8.94 Hz, 1H]; 7.56 [m, 3H]; 7.85 [d, *J* = 8.81 Hz, 1H]; 7.93 [d, *J* = 8.98 Hz, 1H]; 8.24 [d, *J* = 2.52 Hz, 1H]; 8.53 [m, 2H]. ^{13}C NMR ($CDCl_3$): δ 101.9; 113.5; 119.0; 126.3; 126.9; 129.4[d]; 129.7[d]; 129.7; 131.9; 132.1; 132.3; 135.9; 144.6; 151.5; 155.9; 159.4. IR (KBr) cm^{-1}: 1727.2 (C=O), 1625.7 (C=N), 3422.3 (O–H). Elem. anal.: cal. %C = 74.73; %H = 4.32; %N = 4.84; exp. %C = 73.80; %H = 3.99; %N = 4.85.

*2.2.12. 2-Phenyl-9-N,N-dimethylamino-3H-naphtho[2,1-b][1,4]-oxazin-3-one (**12**)*

^{1}H NMR ($CDCl_3$): δ 3.20 [s, 3H]; 7.12 [d, *J* = 8.81 Hz, 1H]; 7.19 [dd, *J* = 8.05 Hz, *J* = 2.58 Hz, 1H]; 7.56 [m, 3H]; 7.75 [d, *J* = 9.06 Hz, 1H]; 7.80 [d, *J* = 8.81 Hz, 1H]; 7.96 [d, *J* = 2.39 Hz, 1H]; 8.51 [m, 2H]. ^{13}C NMR ($CDCl_3$): δ 41.2; 101.6; 112.8; 118.8; 125.7; 126.2; 128.4[d]; 129.3[d]; 129.7; 131.1; 132.1; 132.3; 134.6; 146.5; 148.9; 155.0; 159.8. IR (KBr) cm^{-1}: 1723.9 (C=O), 1626.8 (C=N). Elem. anal.: cal. %C = 75.93; %H = 5.10; %N = 8.86; exp. %C = 75.58; %H = 5.14; %N = 9.38.

*2.2.13. 2-Methyl-3H-naphtho[2,1-b][1,4]-oxazin-3-one (**13**)*

^{1}H NMR ($CDCl_3$): δ 2.65 [s, 3H]; 7.36 [d, *J* = 8.99 Hz, 1H]; 7.58 [t, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H]; 7.68 [t, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H]; 7.88 [t, *J* = 9.74 Hz, *J* = 9.74 Hz, 2H]; 8.77 [d, *J* = 7.9 Hz, 1H]. ^{13}C NMR ($CDCl_3$): δ 21.8; 116.2; 123.1; 126.2; 126.9; 128.3; 128.4; 130.5; 131.3; 131.9; 144.9; 153.8; 154.2. IR (KBr) cm^{-1}: 1726.8 (C=O), 1507.1 (C=N), 1085.3 (C–CH_3). Elem. anal.: cal. %C = 73.92; %H = 4.29; %N = 6.63; exp. %C = 74.22; %H = 4.34; %N = 7.13.

*2.2.14. 2-Methyl-9-methoxy-3H-naphtho[2,1-b][1,4]-oxazin-3-one (**14**)*

^{1}H NMR ($CDCl_3$): δ 2.67 [s, 3H]; 4.01 [s, 3H]; 7.19 [dd, 1H]; 7.21 [d, *J* = 8.9 Hz, 1H]; 7.75 [d, *J* = 8.92 Hz, 1H]; 7.82 [d, *J* = 8.9 Hz, 1H]; 8.06 [d, *J* = 2.42 Hz, 1H]. ^{13}C NMR ($CDCl_3$): δ 21.3; 55.5; 101.1; 113.0; 119.0; 125.0; 126.2; 129.5; 131.1; 131.8; 145.2; 153.5; 153.9; 159.5. IR (KBr) cm^{-1}: 1724.2 (C=O), 1626.4 (C=N), 1272.3 (C–O), 1085.3 (C–CH_3). Elem. anal.: cal. %C = 69.70; %H = 4.60; %N = 5.81; exp. %C = 69.36; %H = 4.73; %N = 6.16.

*2.2.15. 2-Methyl-9-hydroxy-3H-naphtho[2,1-b][1.4]-oxazin-3-one (**15**)*

^{1}H NMR ($CDCl_3$): δ 2.67 [s, 3H]; 5.35 [s, 1H]; 7.19 [dd, 1H]; 7.21 [d, *J* = 8.9 Hz, 1H]; 7.75 [d, *J* = 8.92 Hz, 1H]; 7.82 [d, *J* = 8.9 Hz, 1H]; 8.06 [d, *J* = 2.42 Hz, 1H]. ^{13}C NMR ($CDCl_3$): δ 21.3; 101.1; 113.1; 118.9; 125.0; 126.4; 129.5; 131.1; 131.8; 145.2; 153.3; 154.8; 159.5. IR (KBr) cm^{-1}: 3412.5 (O–H), 1714.5 (C=O), 1634.3 (C=N), 1085.3 (C–CH_3). Elem. anal.: cal. %C = 68.72; %H = 3.99; %N = 6.16; exp. %C = 67.89; %H = 4.33; %N = 6.85.

*2.2.16. 2-Methyl-9-N,N-dimethylamino-3H-naphtho[2,1-b][1,4]-oxazin-3-one (**16**)*

^{1}H NMR ($CDCl_3$): δ 2.56 [s, 3H]; 3.08 [s, 6H]; 6.96 [d, *J* = 8.79 Hz, 1H]; 7.08 [dd, *J* = 9.66 Hz, *J* = 2.58 Hz, 1H]; 7.42 [d, *J* = 2.58 Hz, 1H]; 7.62 [d, *J* = 9.15 Hz, 1H]; 7.64 [d, *J* = 8.79 Hz, 1H]. ^{13}C NMR ($CDCl_3$): δ 21.7; 40.6; 109.5; 111.1; 115.7; 123.99; 124.9; 129.4; 131.7; 132.3; 145.9; 150.2; 151.5; 154.6. IR (KBr) cm^{-1}: 1721.6 (C=O), 1624.9 (C=N). Elem. anal.: cal. %C = 70.85; %H = 5.55; %N = 11.02; exp. %C = 70.89; %H = 6.01; %N = 9.89.

*2.2.17. 2-Phenyl-3H-naphtho[2,1-b][1,4]-oxazin-3-one-6-sulfonic acid (**17**)*

^{1}H NMR (DMSO-d_6): δ 7.41 [m, 1H]; 7.49 [dd, *J* = 6.99 Hz, *J* = 7.61 Hz, 1H]; 7.59 [dd, *J* = 7.01 Hz, *J* = 8.18 Hz, 1H]; 7.72 [s, 1H]; 7.85 [m, 2H]; 7.99 [m, 2H]; 8.88 [d, *J* = 8.2 Hz, 1H]; 9.32 [d, *J* = 7.6 Hz, 1H]; 11.02 [s, 1H]. ^{13}C NMR (DMSO-d_6): δ 111.3; 120.1; 125.8; 126.4; 127.7[d]; 127.9[d]; 130.0; 130.1; 130.4; 130.6; 130.9; 142.7; 143.7; 158.5; 159.9. IR (KBr) cm^{-1}: 1731.2 (C=O), 1635.8 (C=N), 1200.3 (S=O). Elem. anal.: cal. %C = 61.18; %H = 3.14; %N = 3.96; %S = 9.07; exp. C = 61.59%; H = 3.51%; N = 4.06%; S = 8.85%.

*2.2.18. 3-Phenyl-8-hydroxy-2H-naphtho[1,2-b][1,4]-oxazin-2-one (**18**)*

^{1}H NMR ($CDCl_3$): δ 4.19 [s, 1H]; 6.81 [dd, *J* = 2.6 Hz, *J* = 8.96 Hz, 1H]; 6.97 [d, *J* = 2.6 Hz, 1H]; 7.48 [m, 2H]; 7.63 [d, *J* = 8.37, 1H]; 7.76 [m, 2H]; 7.98 [m, 3H]. ^{13}C NMR ($CDCl_3$): δ 106.4; 115.9; 119.0; 120.1; 121.8; 123.8; 126.0; 127.7; 129.7; 130.3; 132.9; 133.9; 152.8; 154.1; 156.3; 160.6. IR (KBr) cm^{-1}: 3422.3 (O–H), 1727.2 (C=O), 1625.7 (C=N). Elem. anal.: cal. %C = 74.73; %H = 4.32; %N = 4.84; exp. C% = 74.12; %H = 3.88; %N = 5.30.

*2.2.19. 3-Phenyl-2H-naphtho[2,3-b][1,4]-oxazin-2-one (**19**)*

^{1}H NMR ($CDCl_3$): δ 7.58 [m, 5H]; 7.70 [s, 1H]; 7.9 [d, 1H, *J* = 8.19 Hz]; 8.01 [d, 1H, *J* = 8.19 Hz]; 8.39 [m, 3H]. ^{13}C NMR ($CDCl_3$): δ 112.3; 126.0; 127.4; 128.4[d]; 128.5; 128.9; 129.2; 129.6[d]; 130.8; 131.0; 131.5; 134.0; 134.3; 144.2; 151.1; 152.2. IR (KBr): cm^{-1} 1724 (C=O); 1639 (C=N). Elem. anal.: cal. %C: 79.11%; %H: 4.06; %N: 5.13; exp. %C: 78.99; %H: 4.03; %N: 5.40.

*2.2.20. 3-Phenyl-2H-naphtho[1,2-b][1,4]-oxazin-2-one (**20**)*

^{1}H NMR ($CDCl_3$): δ 7.53 [m, 3H]; 7.65 [m, 2H]; 7.77 [d, 1H, *J* = 8.81 Hz]; 7.83 [d, 1H, *J* = 8.78 Hz]; 7.89 [m, 1H]; 8.42 [m, 2H]; 8.48 [m, 2H]. ^{13}C NMR ($CDCl_3$): δ 115.7; 122.1; 122.6; 125.5; 125.6; 126.3; 127.3; 127.9; 128.0; 128.4; 128.7; 129.3; 131.3; 134.3; 134.4; 142.6; 150.0; 152.4. IR (KBr): cm^{-1} 1724 (C=O); 1639 (C=N). Elem.

Table 1
Summary of photophysical parameters for the singlet state in benzene as solvent

Compounds	λ_{max}^{Abs} (nm)	ε (M^{-1} cm^{-1})	λ_{max}^{Em}	Φ_F	τ_S^0 (ns)
(**1**)	332	15100 ± 370	450	0.010 ± 0.001	
(**2**)	344	17400 ± 410	440	0.010 ± 0.001	
(**3**)	372	22200 ± 520	444	0.076 ± 0.004	2.5 ± 0.1
(**4**)	374	18600 ± 400	448	0.297 ± 0.015	
(**5**)	402	19300 ± 440	480	0.697 ± 0.035	3.0 ± 0.1
(**6**)	436	18500 ± 390	500	0.526 ± 0.023	
(**7**)	398	19000 ± 480	460	0.460 ± 0.024	2.6 ± 0.1
(**8**)	404	18300 ± 390	465	0.478 ± 0.021	2.9 ± 0.2
(**9**)	410	20700 ± 510	480	0.577 ± 0.029	2.1 ± 0.1
(**10**)	404	16700 ± 280	488	0.668 ± 0.032	5.4 ± 0.3
(**11**)	406	6100 ± 140	486	0.606 ± 0.030	4.8 ± 0.2
(**12**)	474	8900 ± 230	608	0.152 ± 0.006	7.2 ± 0.4
(**13**)	364	10300 ± 300	424	0.198 ± 0.009	1.5 ± 0.1
(**14**)	368	9300 ± 310	461	0.438 ± 0.020	5.5 ± 0.2
(**15**)	370	8200 ± 270	461	0.358 ± 0.016	3.9 ± 0.2
(**16**)	426	8900 ± 240	564	0.084 ± 0.004	
(**17**)	398[a]	13400[a] ± 310	480	0.600[a] ± 0.026	4.5[a] ± 0.2
(**18**)	406	17100 ± 390	487	0.604 ± 0.025	
(**19**)	356	23100 ± 550	514	0.002 ± 0.001	1.2 ± 0.1
(**20**)	396	12370 ± 280	468	0.534 ± 0.018	6.0 ± 0.4
(**21**)	369	13500 ± 260	424	0.017 ± 0.001	

[a] In acetonitrile as solvent.

anal.: cal. %C: 79.11; %H: 4.06; %N: 5.13; exp. %C: 79.08; %H: 4.14; %N: 5.39.

*2.2.21. 1-Methyl-3-phenylquinoxalin-2(1H)-one (**21**)*

1-Methyl-3-phenylquinoxalin-2(1H)-one (**21**) was synthesized according to previously described procedure [57]. ^{1}H NMR ($CDCl_3$): δ 3.73 [s, 3H]; 7.24–740 [m, 4H]; 7.68 [d, 1H, *J* = 8.1 Hz]; 7.76 [d, 1H, *J* = 8.2 Hz]; 7.90 [m, 1H]; 8.38 [m, 2H]. IR (KBr): cm^{-1} 1688 (C=O); 1615 (C=N). Elem. anal.: cal. %C: 76.25; %H: 5.11; %N: 11.85; exp. %C: 76.03; %H: 4.75; %N: 11.89.

3. Results and discussion

3.1. Absorption and fluorescence spectra

The absorption spectra of compounds (**1**)–(**21**) are nearly independent on solvent polarity. Compound (**1**) exhibits the maximum of the lowest-energy absorption band (λ_{max}^{Abs}) in benzene centered at 332 nm (Table 1). However, the inclusion of electron donor substituents in the aromatic ring of benzoxazinone derivatives produces an important bathochromic shift, accordingly, the λ_{max}^{Abs} for compound (**6**) appears around 436 nm in the same solvent. Identical effect was observed in the naphthoxazinone derivatives series. For compound (**7**), λ_{max}^{Abs} in benzene was observed at 398 nm whereas for the 9-*N*,*N*-dimethylamino derivative (**12**) the absorption maximum shifts to 474 nm. Spectra calculations employing DFT formalism (B3LYP/6-311 + G* for structure optimization) and ZINDO-S to calculate the Franck-Condon transitions overestimate λ_{max} by about of 20 nm, however the analysis of molecular orbital indicates a π–π* transition in all cases. The results obtained are comparable to those reported for benzoxazinone derivatives [34,58] and structurally related compounds such as coumarins [59]. Values of λ_{max}^{Abs} and molar absorption coefficient (ε) are collected in Table 1. Data in Table 1 show that naphthoxazinone derivatives have larger λ_{max}^{Abs} values than the analogous benzoxazinone and as is expected, 2-methyl substituted compounds have smaller molar absorption coefficients than the corresponding 2-phenyl analogous. On the other hand, the fluorescence spectrum of compounds (**1**)–(**21**) is strongly dependent on the substrate structure and the polarity of the solvent, such as has been previously reported for several compounds belonging to the same family [33–35,45]. For example we found that the red shift is quite large in polar solvents: for compound (**6**), the position of the emission maximum (λ_{max}^{Em}) shifts from 450 nm in *n*-hexane to 524 nm in methanol, while for compound (**12**), shifts from 524 nm in *n*-hexane to 697 nm in acetonitrile. The red shift can be interpreted in terms of an increased dipole moment of the naphthoxazinones upon chromophore excitation and subsequent solvent relaxation. Representative values of λ_{max}^{Em} and fluorescence quantum yields (Φ_F) in benzene as solvent are collected in Table 1.

The fluorescence quantum yields, Φ_F, for compounds (**1**)–(**3**), (**12**), (**16**), (**19**) and (**21**) in benzene as solvent are very low and remain lower than 0.1 in solvents of different polarities with exception of the naphthoxazinone (**16**) for which a significant increase was observed in hexane as solvent. In contrast, the remaining ones have fluorescence quantum yields in the range 0.2–0.8. For these compounds, the Φ_F value increases or decreases in different extents as the solvent polarity increases. This behavior can be explained in term of both, the energy gap between the T_n (*n*, π*) and S_1(π, π*) states [58] and the structural and energetic factors that contribute to the aromaticity extension [60,61]. Values of the fluorescence lifetime in benzene, measured by employing the phase demodulation method or time-resolved single photon counting, are likewise collected in Table 1. Fluorescence data indicates that the inclusion of the heterocyclic ring produces substantial differences when the same parameters for the aromatic compounds, benzene, anthracene and phenanthrene, are considered. Anthracene fluorescence lifetime is a factor two larger than those reported for phenanthrene. Naphthoxazinone derivatives show an opposite trend, being larger the parameters for the phenanthrene-like compounds than those determined for the anthracene-like oxazinones.

3.2. Singlet oxygen quantum Yields, Φ_Δ

Albeit weak, $O_2(^1\Delta_g)$ NIR phosphorescence provides the most convenient method for the direct monitoring of this specie under steady-state or time-resolved regimes [62–67]. The $O_2(^1\Delta_g)$ phosphorescence decay traces observed in the various solvents by time-resolved detection (TRPD) could be fitted with single exponential functions from which $O_2(^1\Delta_g)$ lifetimes, τ_Δ, could be

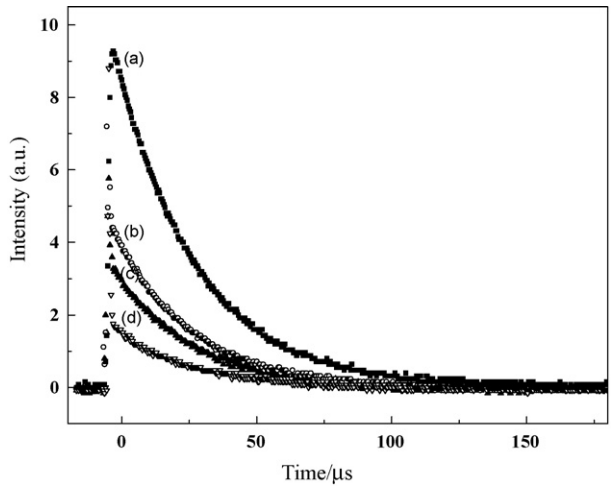

Fig. 2. Singlet oxygen phosphorescence decays observed of PHN (a), (**19**) (b), (**7**) (c) and (**20**) (d), after excitation with 355 nm laser pulses. Compounds were matched at absorbance 0.204 (355 nm).

derived. Within experimental error, the value of τ_Δ in a given solvent remained constant when the different heterocyclic compounds (**1**)–(**21**) and phenalenone, PHN, were used for TRPD.

Fig. 2 shows the singlet oxygen luminescence signals recorded in benzene at 1275 nm for phenalenone employed as the reference and several oxazinone derivatives, after excitation with the third harmonic of a Nd:YAG laser (355 nm). In addition, observed singlet oxygen lifetime does not depend on the laser power and the substrate concentrations used in our experiments. These results indicate that no occurs secondary processes under our experimental conditions.

Singlet oxygen quantum yields were determined by comparison of the time zero signal intensity, I_0, of luminescence decay observed for the studied compound and phenalenone employed as the reference. Such as the singlet oxygen lifetime, the calculated Φ_Δ values were independent of laser power in the range between 5 and 30 mJ per pulse and sensitizer absorbance between 0.1 and 0.33. Representative experiments for compounds (**7**), (**19**), (**20**) and (**21**), employing benzene as solvent are shown in Fig. 3. The values

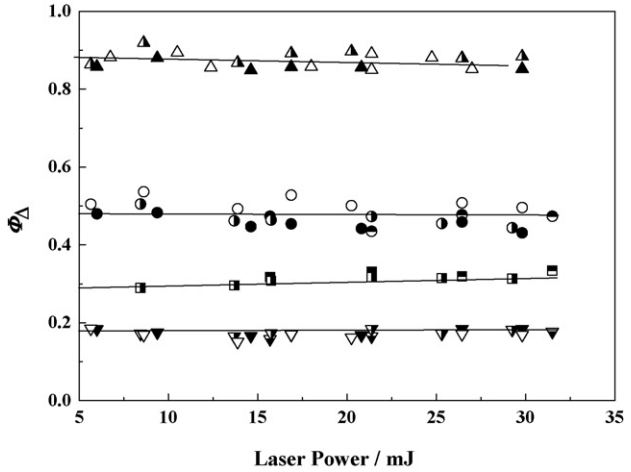

Fig. 3. Singlet oxygen quantum yield dependence on the laser power and the sensitizer absorbance for compounds (**7**) (■), (**19**) (●), (**20**) (▼) and (**21**)(▲). Filled symbol A = 0.103 (355 nm); semi-filled symbol A = 0.204 (355 nm); clear symbol A = 0.332 (355 nm).

Table 2
Quantum yields of singlet oxygen generation by the oxazinone derivatives (**1**)–(**20**) and quinoxalinone (**21**) in solvents representative of the polarity scale

Oxazinone	Φ_Δ		
	Benzene	Acetonitrile	Methanol
(**1**)	0.27 ± 0.01	0.28 ± 0.01	0.27 ± 0.01
(**2**)	0.45 ± 0.02	0.32 ± 0.01	0.27 ± 0.01
(**3**)	0.32 ± 0.01	0.22 ± 0.01	0.03 ± 0.01
(**4**)	0.59 ± 0.03	0.48 ± 0.02	0.42 ± 0.02
(**5**)	0.12 ± 0.01	0.11 ± 0.01	0.06 ± 0.01
(**6**)	0.09 ± 0.01	–	0.06 ± 0.01
(**7**)	0.28 ± 0.01	0.22 ± 0.01	0.16 ± 0.01
(**8**)	0.21 ± 0.01	0.25 ± 0.01	0.20 ± 0.01
(**9**)	0.18 ± 0.01	0.14 ± 0.01	0.10 ± 0.01
(**10**)	0.14 ± 0.01	0.18 ± 0.01	0.11 ± 0.01
(**11**)	0.13 ± 0.01	0.14 ± 0.01	–
(**12**)	0.18 ± 0.01	–	0.12 ± 0.01
(**13**)	0.79 ± 0.04	0.53 ± 0.03	0.44 ± 0.02
(**14**)	0.51 ± 0.03	0.33 ± 0.02	–
(**15**)	0.13 ± 0.01	–	0.11 ± 0.01
(**16**)	–	–	–
(**17**)	0.23 ± 0.01	0.20 ± 0.01	0.19 ± 0.01
(**18**)	0.11 ± 0.01	0.09 ± 0.01	0.07 ± 0.01
(**19**)	0.48 ± 0.02	0.48 ± 0.02	0.33 ± 0.01
(**20**)	0.18 ± 0.01	0.21 ± 0.01	0.14 ± 0.01
(**21**)	0.88 ± 0.07	0.84 ± 0.06	0.76 ± 0.04

of singlet oxygen quantum yields in solvents with a wide range of polarities, extrapolated to laser power and sensitizer concentration equal to zero, are reported in Table 2.

The larger singlet oxygen quantum yields for compounds (**2**), (**4**), (**13**), (**14**), (**19**) and (**21**) can be explained in terms of an efficient intersystem-crossing process. From semiempirical calculations it has been suggested that for coumarins, quinoxalinones and benzoxazinones, the intersystem crossing from the S_1 (π, π^*) state to the T_n (n, π^*) state competes with the fluorescence, and their Φ_F values can be predicted by calculating the ΔE (T_n (n, π^*), S_1 (π, π^*)) values (the energy gap between the T_n (n, π^*) and S_1 (π, π^*) states). The compounds having a higher T_n (n, π^*) state (the lowest triplet n, π^* state) than the S_1(π, π^*) state (the fluorescent state) strongly fluoresce [68]. A comparison of the B3LYP-6311g + calculations for compounds (**7**), (**19**) and (**20**), shows that the compounds (**7**) and (**20**) have extensive delocalization of HOMO and LUMO involving the naphthalene moiety, the oxazinone ring and the phenyl substituent. For (**19**) was found that HOMO is mainly localized on the oxazinone ring and the neighbor condensed aromatic ring without contribution of phenyl substituent. Consequently, from the aromaticity point of view, intersystem crossing must be more efficient for compound (**19**) as was found experimentally. Furthermore, within the limitations of ZINDO calculations conducted in vacuo, for the naphthoxazinone derivative (**19**) was found that the energies of the higher T_n (n, π^*) states (T_4, T_5 and T_6) are lower than the energy of the S_1 (π, π^*) state whereas for compounds (**1**) and (**3**), T_3 is the lower triplet which energy is near to the S_1 (π, π^*) state. These calculations support a larger triplet quantum yield concomitant with a larger singlet oxygen quantum yield for (**19**) than that (**7**) and (**20**), due to the larger spin-orbit coupling for S_1 (π, π^*) → T_n (n, π^*) transitions.

3.3. Photostability

As was aforementioned, high stability to irradiation is an essential requirement for a molecule to behave as a good singlet oxygen sensitizer. We evaluate the photostability of all compounds of the series in long-term irradiation conditions by observing the changes in its GC–MS chromatogram and/or its UV–vis spectra in benzene

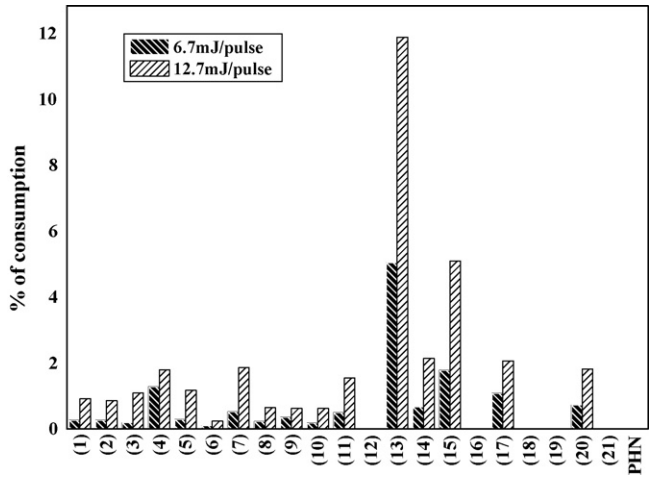

Fig. 4. Consumption (%) of the oxazinone derivatives (**1**)–(**20**), quinoxalinone (**21**) and PHN, after 500 laser pulses.

as solvent after 500 laser pulses at two different laser powers. The results obtained are shown in Fig. 4.

The data of Fig. 4 indicate that 2-methyl substituted naphtoxazinones (**13**), (**14**) and (**15**) are the most photoreactive compounds, decomposing in 11.88, 2.13 and 5.09% (see also Appendix A) when are irradiated with 500 laser pulses of an energy of 12.7 mJ per pulse. Considering that photostability was evaluated in long-term irradiation experiments, these results would be explained in terms of singlet oxygen reaction with the substrate and/or by photoreactions from the singlet excited state. Nishio and Omote [46] and Koch et al. [69] have reported that methylbenzoxazinones and methyloxazinones react, in the absence of additives, from triplet state to give reductive dimers, however in our experimental conditions reactions from triplet excited state are very improbable because the efficient triplet quenching by oxygen. Surprisingly, the 9-*N*,*N*-dimethyl derivative (**16**), neither shows appreciable fluorescence (Φ_F (benzene) = 0.084) nor produces singlet molecular oxygen. In addition, it is photostable even in the long-term irradiation conditions employed to test its photoconsumption. The same result was found for compound (**12**), the 9-*N*,*N*-dimethyl-2-phenyl naphthoxazinone derivative. In addition, for (**12**) and (**16**) we measure the triplet quantum yields (Φ_T) in benzene, employing the classical method of 1,3-pentadiene photoisomerization [51] with benzophenone as actinometer ($\Phi_T = 1$ [70]). Values of Φ_T equal to 0.20 ± 0.003 and 0.003 ± 0.003 (within the experimental error) were found for (**12**) and (**16**), respectively. These data indicate that singlet oxygen is produced probably from the triplet excited state and the low singlet oxygen quantum yield observed for (**12**) and (**16**) cannot be explained in terms of singlet oxygen quenching by the tertiary amino substituents. For these compounds, a different decay path involving the dimethylamino group, can explain their very different photochemical behavior. As in the nearly related coumarins derivatives, the presence of the dimethylamino (donor) and iminolactone (acceptor) groups in (**12**) and (**16**), separated by the conjugate naphthalene ring, leads to a dipolar, nearly planar intramolecular charge transfer state, which results in a great increase in dipole moment concomitant with a decrease in emission and a strong red shift of λ_{max}^{Em}. For compounds (**12**) and (**16**) the fluorescence quantum yield diminished from 0.721 and 0.603 in hexane to 0.014 and 0.011 in methanol, respectively. Furthermore, λ_{max}^{Em} of (**12**) and (**16**) shows a bathochromic shift of 146 and 114 nm in the same solvents. On the other hand, it was shown that this behavior is strongly reduced when the amino substituent is included in a rigid nearly planar ring. For example, coumarine 152A have a amino group freely rotating and fluorescence quantum yield in ethanol equal to 0.08 whereas coumarine 153 that include an amino substituent in a rigid structure have a fluorescence quantum yield of 0.41 [36]. This effect can be explained in terms of the rotation of the amino substituents that contribute to the energy dissipation leading in some cases to the formation of a non-planar twisted intramolecular charge transfer state [71–73]. A somewhat different behavior was found for 7-amino and 7-*N*,*N*-dimethylamino derivatives of 2-phenylbenzoxazinone. For these compounds, we measure a small singlet oxygen quantum yield and found that they are very photostable, but also they show elevated fluorescence quantum yields. This behavior can be ascribed to the smaller contribution of the amino or dimethylamino group rotation to the energy dissipation of the lower singlet excited state in the benzoxazinone derivatives [74].

The most appropriate molecules in the series as singlet oxygen sensitizers are compounds (**2**), (**4**), (**19**) and (**21**). The benzoxazinone derivatives (**2**) and (**4**), exhibit large Φ_Δ values in the studied solvents, but photodecompose between 1 and 2% in benzene. The lineal naphthoxazinone (**19**) and the quinoxalinone derivative (**21**) are the compounds that accomplish all the requisites to be a good singlet oxygen sensitizer. They have molar absorbilities of 23100 ± 550 and 13500 ± 260 at λ_{max}^{Abs}, respectively, and a relatively wide low energy absorption band (between 300 and 400 nm). Also, phosphorescence measurements in a heavy atom containing solvent for compound (**19**), allow us to estimate a triplet energy level of 188 ± 5 kJ mol^{-1} and from laser flash photolysis experiments we measure a triplet lifetime equal to 36 μs. More favourable triplet photophysical parameters are expected for quinoxalinone (**21**) for which a triplet quantum yield equal to 1.06 has been previouly reported [75]. Photophysical properties of (**19**) in addition to its high photostability in air equilibrated and oxygen saturated solutions even in the presence of electron donating additives such as triethylamine (same behavior has been reported for (**21**) [76], make these compounds almost an ideal sensitizer to produce singlet molecular oxygen in a wide diversity of media.

4. Conclusions

The photophysics of aryloxazinone-derivatives studied in this work and consequently its capacity to produce singlet molecular oxygen is strongly dependent on the type of aromatic ring fused to the heterocycle, and in the naphthalene derivarives series on the relative position of the oxazinone ring on the naphthalene moiety. Furthermore, subtituents in the imino double bond and in the aromatic system plays an important role in determining the photophysical properties. 2-Phenyl-*p*-substituted benzoxazinone derivatives produce excited oxygen in moderate quantum yields. Inclusion of electron donors groups in the aromatic ring increases significantly the emission from the excited singlet state with a concomitant diminution in the ability to produce singlet oxygen. 2-Phenyl and 2-methyl naphthoxazinones derivatives are more fluorescent than the compounds of the corresponding benzo series, and generate singlet molecular oxygen in low to moderate yields. The most efficient compounds to be employed as singlet oxygen sensitizers are the anthracene like 3-phenyl-2H-naphtho[2,3-b][1,4]-oxazin-2-one (**19**) and the 1-methyl-3-phenylquinoxalin-2(1H)-one (**21**). These compounds are photostable in the absence and the presence of electron donor additives under large doses of irradiation, accomplishing all requisites to be good sensitizer and to produce singlet oxygen in high yields, almost independently on solvent polarity.

Acknowledgements

Financial support from FONDECYT (grant 1050796) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.06.014.

References

[1] F. Wilkinson, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 22 (1993) 113–262.
[2] M.C. DeRosa, R.J. Crutchley, Coordin. Chem. Rev. 233–234 (2002) 351–371.
[3] R. Schmidt, Photochem. Photobiol. 82 (2006) 1161–1177.
[4] A. Karotki, M. Kruk, M. Drobizhev, A. Rebane, E. Nickel, C.W. Spangler, J. Sel. Top. Quant. Elect. 7 (2001) 971–975.
[5] P.K. Frederiksen, M. Jorgensen, P.R. Ogilby, J. Am. Chem. Soc. 123 (2001) 1215–1221.
[6] P.K. Frederiksen, S.P. McIlroy, C.B. Nielsen, L. Nikolajsen, E. Skovsen, M. Jorgensen, K.V. Mikkelsen, P.R. Ogilby, J. Am. Chem. Soc. 127 (2005) 255–269.
[7] S.P. McIlroy, E. Clo, L. Nikolajsen, P.K. Frederiksen, C.B. Nielsen, K.V. Mikkelsen, K.V. Gothelf, P.R. Ogilby, J. Org. Chem. 70 (2005) 1134–1146.
[8] J. Arnbjerg, M.J. Paterson, C.B. Nielsen, M. Jorgensen, O. Christiansen, P.R. Ogilby, J. Phys. Chem. A 111 (2007) 5756–5767.
[9] J. Arnbjerg, A. Jimenez-Banzo, M.J. Paterson, S. Nonell, J.I. Borrell, O. Christiansen, P.R. Ogilby, J. Am. Chem. Soc. 129 (2007) 5188–5199.
[10] J. Arnbjerg, M. Johnsen, P.K. Frederiksen, S.E. Braslavsky, P.R. Ogilby, J. Phys. Chem. A 110 (2006) 7375–7385.
[11] D. Severino, H.C. Junqueira, M. Gugliotti, D.S. Gabrielli, M.S. Baptista, Photochem. Photobiol. 77 (2003) 459–468.
[12] K. Gollnick, T. Franken, M.F.R. Fouda, H.R. Paur, S. Held, J. Photochem. Photobiol. B:Biol. 12 (1992) 57–81.
[13] P. Bilski, R. Dabestani, C.F. Chignell, J. Phys. Chem. 95 (1991) 5784–5791.
[14] A.A. Abdel-Shafi, D.R. Worrall, F. Wilkinson, J. Photochem. Photobiol. A: Chem. 142 (2001) 133–143.
[15] A.A. Abdel-Shafi, F. Wilkinson, J. Phys. Chem. A 104 (2000) 5747–5757.
[16] A.A. Abdel-Shafi, D.R. Worrall, J. Photochem. Photobiol. A: Chem. 172 (2005) 170–179.
[17] I. Gutierrez, S.G. Bertolotti, M.A. Biasutti, A.T. Soltermann, N.A. Garcia, Can. J. Chem. 75 (1997) 423–428.
[18] A.E. Alegria, A. Ferrer, G. Santiago, E. Sepulveda, W. Flores, J. Photochem. Photobiol. A: Chem. 127 (1999) 57–65.
[19] Z.J. Diwu, Photochem. Photobiol. 61 (1995) 632–638.
[20] S.C.N. Montoya, L.R. Comini, M. Sarmiento, C. Becerra, I. Albesa, G.A. Arguello, J.L. Cabrera, J. Photochem. Photobiol. B: Biol. 78 (2005) 77–83.
[21] C. Flors, P.R. Ogilby, J.G. Luis, T.A. Grillo, L.R. Izquierdo, P.L. Gentili, L. Bussotti, S. Nonell, Photochem. Photobiol. 82 (2006) 95–103.
[22] E. Oliveros, S.H. Bossmann, S. Nonell, C. Marti, G. Heit, G. Troscher, A. Neuner, C. Martinez, A.M. Braun, New J. Chem. 23 (1999) 85–93.
[23] C. Schweitzer, Z. Mehrdad, A. Noll, E.W. Grabner, R. Schmidt, J. Phys. Chem. A 107 (2003) 2192–2198.
[24] N. Rubio, F. Prat, N. Bou, J.I. Borrell, J. Teixido, A. Villanueva, A. Juarranz, M. Canete, J.C. Stockert, S. Nonell, New J. Chem. 29 (2005) 378–384.
[25] H. Shinohara, O. Tsaryova, G. Schnurpfeil, D. Wohrle, J. Photochem. Photobiol. A: Chem. 184 (2006) 50–57.
[26] C.M. Allen, W.M. Sharman, C. La Madeleine, J.M. Weber, R. Langlois, R. Ouellet, J.E. van Lier, Photochem. Photobiol. 70 (1999) 512–523.
[27] J.D. Spikes, J.E. Vanlier, J.C. Bommer, J. Photochem. Photobiol. A: Chem. 91 (1995) 193–198.
[28] M. Soncin, A. Busetti, R. Biolo, G. Jori, G. Kwag, Y.S. Li, M.E. Kenney, M.A.J. Rodgers, J. Photochem. Photobiol. B: Biol. 42 (1998) 202–210.
[29] M. Pineiro, M.M. Pereira, A.M.D.R. Gonsalves, L.G. Arnaut, S.J. Formosinho, J. Photochem. Photobiol. A: Chem. 138 (2001) 147–157.
[30] X.F. Shan, T.Y. Wang, S.Y. Li, L.Y. Yang, L.M. Fu, G.Q. Yang, Z.P. Wang, J.S. Ma, J. Photochem. Photobiol. B: Biol. 82 (2006) 140–145.
[31] S. Fukuzumi, K. Ohkubo, X. Zheng, Y. Chen, R.K. Pandey, R. Zhan, K.M. Kadish, J. Phys. Chem. B 112 (2008) 2738–2746.
[32] M. Pineiro, A.M.D.R. Gonsalves, M.M. Pereira, S.J. Formosinho, L.G. Arnaut, J. Phys. Chem. A 106 (2002) 3787–3795.
[33] M.T. Le Bris, J. Heterocyclic Chem. 21 (1984) 551–555.
[34] M.T. Le Bris, J. Heterocyclic Chem. 22 (1985) 1275–1280.
[35] M.T. Le Bris, J. Mugnier, J. Boursons, B. Valeur, Chem. Phys. Lett. 1 (1985) 124–127.
[36] M.T. Le Bris, J. Heterocyclic Chem. 26 (1989) 429–433.
[37] F. Dupuy, C. Rullière, M.T. Le Bris, B. Valeur, Opt. Commun. 51 (1984) 36–40.
[38] J. Mugnier, Y. Dordet, J. Pouget, M.T. Le Bris, B. Valeur, Sol. Energy Mater. 15 (1987) 65–75.
[39] M. Monsigny, P. Midoux, M.T. Le Bris, A.C. Roche, B. Valeur, Biol. Cell 67 (1989) 193–200.
[40] M. Monsigny, P. Midoux, C. Depierreux, C. Bebear, M.T. Le Bris, B. Valeur, Biol. Cell 70 (1990) 101–105.
[41] C. Depierreux, M.T. Le Bris, M.F. Michel, B. Valeur, M. Monsigny, F. Delmotte, FEMS Microbiol. Lett. 67 (1990) 237–243.
[42] S. Fery-Forgues, M.T. Le Bris, J.P. Guette, B. Valeur, J. Phys. Chem. 92 (1988) 6233–6237.
[43] S. Fery-Forgues, M.T. Le Bris, J.P. Guette, B. Valeur, J. Chem. Soc. Chem. Commun. 5 (1988) 384–385.
[44] O.I. Khochkina, I.V. Sokolova, L.I. Loboda, Russ. Phys. J. 31 (1988) 510–513.
[45] S. Fery-Forgues, M.T. Le Bris, J.-C. Mialocq, J. Pouget, W. Rettig, B. Valeur, J. Phys. Chem. 96 (1992) 701–710.
[46] T. Nishio, Y. Omote, J. Org. Chem. 50 (1985) 1370–1373.
[47] T. Nishio, J. Chem. Soc., Perkin Trans. I (1990) 565–570.
[48] D.F. Eaton, Pure Appl. Chem. 60 (1988) 1107–1114.
[49] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 991–1024.
[50] C.A. Heller, R.A. Henry, B.A. McLaughlin, D.E. Bliss, J. Chem. Eng. Data 19 (1974) 214–219.
[51] H.J. Kuhn, S.E. Braslavsky, R. Schmidt, Pure Appl. Chem. 76 (2004) 2105–2146.
[52] B.K. Nunnally, H. He, L.-C. Li, S.A. Tucker, L.B. McGown, Anal. Chem. 69 (1997) 2392–2397.
[53] S. Pant, H.B. Tripathi, D.D. Pant, J. Photochem. Photobiol. A: Chem. 81 (1994) 7–11.
[54] R.B. Mofett, J. Med. Chem. 9 (1966) 475–478.
[55] A. Márquez, C. Saitz, A. Cañete, H. Rodríguez, C. Jullian, Mag. Reson. Chem. 36 (1998) 449–453.
[56] C. Saitz, H. Rodríguez, A. Márquez, A. Cañete, C. Jullian, A.L. Zanocco, Synth. Commun. 31 (2001) 135–140.
[57] T. Nishio, J. Org. Chem. 49 (1984) 827–832.
[58] K. Azuma, S. Suzuki, S. Uchiyama, T. Kajiro, T. Santa, K. Imai, Photochem. Photobiol. Sci. 2 (2003) 443–449.
[59] B. Kovac, I. Novak, Spectrochim. Acta 58 (2002) 1483–1488.
[60] T.M. Krygowski, M.K. Cyranski, Tetrahedron 52 (1996) 13795–13802.
[61] T.M. Krygowski, M.K. Cyranski, Chem. Rev. 101 (2001) 1385–1419.
[62] A.U. Khan, Chem. Phys. Lett. 72 (1980) 112–114.
[63] A.A. Krasnovsky, Chem. Phys. Lett. 81 (1981) 443–445.
[64] M.A.J. Rodgers, J. Am. Chem. Soc. 105 (1983) 6201–6205.
[65] A.M. Braun, E. Oliveros, Pure Appl. Chem. 62 (1990) 1467–1476.
[66] E. Oliveros, F. Besançon, M. Boneva, B. Kroutler, A.M. Braun, J. Photochem. Photobiol. B: Biol. 29 (1995) 37–44.
[67] S. Nonell, S.E. Braslavsky, Method. Enzymol. 319 (2000) 37–49.
[68] E. Gikas, M. Parissi-Poulou, M. Kazanis, A. Vavagiannis, J. Mol. Struct.: Theochem. 724 (2005) 135–142.
[69] T.H. Koch, J.A. Olesen, J. DeNiro, J. Org. Chem. 40 (1975) 14–19.
[70] I. Carmichael, G.L. Hug, J. Phys. Chem. Ref. Data 15 (1986) 1–251.
[71] A. Kawski, B. Kuklinski, P. Bojarski, Chem. Phys. Lett. 448 (2007) 208–212.
[72] J. Dobkowski, L. Sazanovich, Acta Phys. Pol. A 112 (2007) 127–142.
[73] T.S. Singh, S. Mitra, J. Lumin. 127 (2007) 508–514.
[74] A. Morimoto, L. Biczok, T. Yatsuhashi, T. Shimada, S. Baba, H. Tachibana, D.A. Tryk, H. Inoue, J. Phys. Chem. A 106 (2002) 10089–10095.
[75] J.R. De la Fuente, A. Cañete, C. Saitz, C. Jullian, J. Phys. Chem. A 106 (2002) 7113–7120.
[76] J.R. De la Fuente, A. Cañete, A.L. Zanocco, C. Saitz, C. Jullian, J. Org. Chem. 65 (2000) 7949–7958.