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# Fluorescence analysis of iodinated acetophenone derivatives

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### HIGHLIGHTS

# G R A P H I C A L A B S T R A C T

Absorbance

Fluorescence

stituents: the fluorescence quantum efficiency increases approximately 60%.

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In the present paper the synthesis and optical characterization of iodinated acetophenone, 4-hydroxy-3-

iodoacetophenone and 4-hydroxy-3,5-diiodoacetophenone obtained from 4-hydroxyacetophenone, were

ior was strongly altered when two iodine atoms (4-hydroxy-3,5-diiodoacetophenone) were acting as sub-

- Two iodinated hydroxyacetophenones were synthetized from 4-hydroxyacetophenone.
  The optical behavior of these iodinated compounds was determined and analyzed.
- The optical properties were strongly altered by the presence of the iodine atom.
- Iodine atoms induced a red shift of the absorption bands.
- Fluorescence quantum yield was also altered by the iodine atoms.

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## Introduction

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<sup>1014</sup> carried out. The optical features of iodinated molecules were determined by performing the UV–Vis absorption, fluorescence and thermal lens spectroscopies. The results showed that the optical properties of the 4-hydroxyacetophenone is altered when the iodine atom is inserted, as substituent, in the aromatic ring. Although it was determined that the optical feature was changed when one iodine atom was inserted in the aromatic ring (4-hydroxy-3-iodoacetophenone), the results revealed that emission behav-

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ABSTRACT

intermediates in organic synthesis, especially by Sonogashira and Suzuki cross-coupling reactions [3,4]. Additionally, iodinated aromatic compounds are also important building blocks used in the synthesis of biologically active products [5], for instance, being usually related to the production of new hormone derivatives in the thyroid gland [6]. In fact, they are widely applied as drugs and diagnostic agents in medicine [7,8].

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As recently reported by Gallo et al. [9], it is possible to obtain significant yields of iodinated aromatic compounds derived from 4-hydroxyacetophenone under mild reaction conditions. This is

lodinated aromatic compounds have been widely used for over a century. They have been utilized as valuable compounds for pharmaceutical and agricultural applications due to their antibacterial and antifungal properties [1,2]. They have also been used as

\* Corresponding author. *E-mail address:* andersoncaires@ufgd.edu.br (A.R.L. Caires). done by using molecular iodine as an iodine source, aqueous hydrogen peroxide as a safe and environmentally accepted oxidizer, and water as a nonflammable and innocuous solvent [10]. The 4-hydroxyacetophenone is commonly used in the plastic, pharmaceutical, agrochemical and cosmetic industries [11]. In addition to these applications, the 4-hydroxyacetophenone has been studied by various spectroscopic techniques for presenting fluorescence, phosphorescence and nonlinear optical properties.

Results obtained by analyzing Raman spectroscopy, infrared, X-ray diffraction, SERS and theoretical simulations have demonstrated that 4-hydroxyacetophenone has great potential to be used in nonlinear optic applications [12,13]. Fluorescence and phosphorescence properties of 4-hydroxyacetophenone were also determined [14,15]. Kearns and Case observed that the phosphorescence transitions are directly related to the inter system crossing process (triplet state population) induced by the presence of substituent groups such as carbonyl groups [14]. In the case of fluorescence, Catalán and co-workers observed that 4-hydroxyacetophenone presented a maximum emission band at 480 nm when excited at 320 nm. According to the authors, this single emission band in the visible range corresponds to the formation of an intramolecular hydrogen bond [15].

4-Hydroxyacetophenone presents good optical properties and was already extensively studied [12–15]. Nevertheless, to the best of our knowledge, there is a lack of information concerning the optical features of the iodinated aromatic compounds obtained from 4-hydroxyacetophenone. Therefore, due to the importance of obtaining iodinated aromatic compounds with relevant optical properties, the present study aimed to synthetize two iodinated hydroxy-3,5-diiodoacetophenone) and characterize its optical properties. UV–Vis absorption, fluorescence and thermal lens spectroscopies were performed in order to analyze the optical behavior of hydroxyacetophenone and iodinated hydroxyacetophenones.

## Materials and methods

lodinated hydroxyacetophenones were synthetized as previously reported by Gallo and co-workers [10]. The 4-hydroxyacetophenone (99.99%) was purchased from Sigma–Aldrich (Brazil) and used as starting material. The 4-hydroxyacetophenone (#1) was reacted with 1.5 equivalents of iodine and 3 equivalents of hydrogen peroxide in water at room temperature for 24 h. 4-hydroxy-3iodoacetophenone (#2) and 4-hydroxy-3,5-diiodoacetophenone (#3) were obtained in a very good yields (Scheme 1).

To a solution of #1 (2.7586 g, 20 mmol) and iodine (7.68 g, 30 mmol) in distilled water (100 mL) was added to hydrogen peroxide (6.4 mL of a 30% (w/v) aqueous solution, 60 mmol). The mixture was stirred at room temperature for 24 h. Afterwards, a 10% (w/v) sodium thiosulfate aqueous solution (100 mL) was added to the mixture, which was extracted with dichloromethane or ethyl acetate ( $3 \times 100$  mL). The organic phase was dried over MgSO<sub>4</sub>. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using dichloromethane as eluent, affording #2 and #3 samples in yields of 65% and 15%, respectively.

UV absorption spectra were collected in the 200–400 nm range by using an absorption spectrophotometer Cary 50 from Varian. The spectrophotometer has a pulsed xenon lamp, a 0.25 m Czerny–Turner monochromator and a Si diode detector. The samples were diluted in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) at  $8.8 \times 10^{-6}$ mol L<sup>-1</sup>. All measurements were performed at room temperature using a quartz cuvette (sample holder) with a 10 mm optical path length and two polished faces.

Fluorescence measurements were performed on a spectrofluorimeter Cary Eclipse from Varian. A pulsed xenon lamp (80 Hz), with half the width of the pulse approximately 2  $\mu$ m and peak power equivalent to 75 kW, was used as an excitation source. Two Czerny–Turner monochromators were used for selecting the excitation and emission wavelengths. The fluorescence signal was detected using a photomultiplier tube (R928). Emission spectra were collected in the 375–600 nm range when excited at 355 nm and excitation spectra were obtained between 250 and 410 nm when emission signal was detected at 430 nm. The samples were diluted in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) at  $4.4 \times 10^{-3}$ mol L<sup>-1</sup>. All measurements were performed at room temperature using a quartz cuvette (sample holder) with a 10 mm optical path length and four polished faces.

Thermal lens (TL) transient signal was obtained in the modemismatched experimental setup by using two lasers: an Ar laser and a HeNe laser operating at  $\lambda_{exc}$  = 361 nm and  $\lambda_p$  = 632.8 nm, respectively. The first laser was used to excite the sample in order to create the TL effect, while the second laser was used to probe the TL effect. All measurements were performed at room temperature using a quartz cuvette with a 1 mm optical path length (*L*) and two polished faces. The samples were added in the cuvette and then placed in the beam waist of the pump laser (Ar laser). After the pump laser energy was absorbed by the sample, a localized change could be observed in the refractive index due the variation in the local temperature, which was detected by the probe laser (HeNe laser).

### **Results and discussion**

The UV absorption analysis showed that the sample #1 presents two maximum bands at around 226 and 265 nm, as shown in Fig. 1a, which involves  $\pi \rightarrow \pi^*$  transitions [12]. In the case of both iodinated hydroxyacetophenones, the results revealed a red shift of these two absorption bands, as presented in Fig. 1b and c. The red shift may be explained by electron delocalization introduced by the presence of the iodine (substituent). The electron delocalization may induce a less antibonding character of the  $\pi^*$  orbital, lowering the energy level of this orbital [16]. In addition, it was also determined a new absorption band at 242 nm for the sample #3.



Scheme 1. Synthesis of iodinated hydroxyacetophenones. The studied samples are named as #1, #2 and #3, as indicated in the scheme.



**Fig. 1.** Absorbance of the: (a) 4-hydroxyacetophenone (sample #1); (b) 4-hydroxy-3-iodoacetophenone (sample #2); and (c) 4-hydroxy-3,5-diiodoacetophenone (sample #3). The samples were diluted in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) at  $8.8 \times 10^{-6} \text{ mol } L^{-1}$ .

The origin of the band at 242 nm may be related to the emergence of a charge transfer band induced by increasing the charge density caused by the iodine. It is well known that a new charge transfer band (electron transfer band) may arise when an electron acceptor substituent is introduced in the aromatic ring [16].

Fig. 2 shows the fluorescence spectra of the 4-hydroxyacetophenone and iodinated hydroxyacetophenones in the



**Fig. 2.** Fluorescence intensity of the: (a) 4-hydroxyacetophenone (sample #1); (b) 4-hydroxy-3-iodoacetophenone (sample #2); and (c) 4-hydroxy-3,5-diiodoacetophenone (sample #3). The samples were excited at 355 nm and diluted in dichloromethane ( $CH_2CI_2$ ) at  $4.4 \times 10^{-3}$  mol L<sup>-1</sup>.

375–600 nm range when excited at 355 nm. The results reveal an enhancement of the fluorescence signal associated with the presence of the iodine in the molecular structure. In fact, the molecule containing two iodine atoms (sample #3) presented a higher enhancement than the molecule with one iodine atom (sample #2). Additionally, the Stokes shifts were also determined by analyzing the excitation and emission spectra. As it can be seen in Fig. 3, the Stokes shift presented a significant change only for the sample #3 in which the determined values are presented in Table 1.

Aiming to understand the fluorescence behavior, a close analysis of the fluorescence quantum yield and absorption changes (at 355 nm – excitation wavelength) was conducted as follows. Table 2 presents the absorption enhancement ratio at 355 nm and the fluorescence enhancement ratio when excited at 355 nm. It was obtained by comparing the 4-hydroxyacetophenone and iodinated hydroxyacetophenones. It is worth pointing out that the fluorescence enhancement was determined by calculating the area under the emission curve. Furthermore, in this analysis, the determination of the molecular absorption at 355 nm was carried out with the same concentration used in the fluorescence measurement (i.e.,  $4.4 \times 10^{-3}$  mol L<sup>-1</sup>). The results show a similar increase in the absorption and fluorescence ratios when one iodine atom was introduced in the molecular structure, where the absorption and fluorescence ratios increased about 1.8 times. This result shows that the fluorescence enhancement was only due to the increase in the absorption. On the contrary, different increases in the absorption and fluorescence ratios were found when two iodine atoms were introduced in the molecular structure. It was found that the fluorescence ratio increase (about 4.30) was higher than the absorption ratio increase (about 2.9). In this case, the fluorescence enhancement cannot only be attributed to the increase in the absorption process. It also revealed that fluorescence quantum yield ( $\Phi_F$ ) increased when two iodine atoms were inserted in the 4-hvdroxvacetophenone.

For the steady-state fluorescence,  $\Phi_F$  can be conveniently expressed in terms of emission spectrum [17]:

$$\int_{0}^{\infty} F_{\lambda}(\lambda_{F}) d\lambda_{F} = \Phi_{F} \tag{1}$$

In which  $F_{\lambda}(\lambda_F)$  represents the distribution of the probability of the transitions from the first excited electronic level to the ground electronic level. In practical situations, the fluorescence intensity



**Fig. 3.** Thermal lens characteristic signal to the 4-hydroxyacetophenone (sample #1) diluted at CH<sub>2</sub>Cl<sub>2</sub> solution  $(4.4 \times 10^{-3} \text{ mol L}^{-1})$ . The sample was excited at 361 nm with 90 mW and the TL signal was probed at 632.8 nm with a HeNe laser. Similar curves were also obtained for samples #2 and #3.

	Ta	ble	1
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Stokes-shift values for samples #1, #2 and #3.

Sample #	Stoke shift (nm)
1	29
3	38

 Table 2

 Absorbance ratio at 355 nm and fluorescence ratio at 430 nm when excited at 355 nm

Sample ratio	Absorption ratio	Fluorescence ratio
#2/#1	1.8	1.8
#3/#1	2.9	4.3

 $I_F(\lambda_F)$  measured at a wavelength  $\lambda_F$  is proportional to  $F_{\lambda}(\lambda_F)$  and to the absorption-related intensity  $I_A(\lambda_E)$  at the excitation wavelength  $\lambda_E$ . Therefore, the  $F_{\lambda}(\lambda_F)$  can be written as:

$$F_{\lambda}(\lambda_F) = \frac{I_F(\lambda_E, \lambda_F,)}{kI_A(\lambda_E)}$$
(2)

where *k* is a constant that depends on several experimental parameters (i.e., the bandwidth of the excitation and emission monochromators, voltage of the photomultiplier tube, solid angle of fluorescence collection, etc.) [17]. Consequently, the  $\Phi_F$  can be expressed by the relationship:

$$\Phi_F = \frac{1}{kI_A(\lambda_E)} \int_0^\infty I_F(\lambda_E, \lambda_F,) d\lambda_F$$
(3)

where  $\int_{0}^{\infty} I_{F}(\lambda_{E}, \lambda_{F}, )d\lambda_{F}$  is obtained by calculating the area under the emission curve, hereafter represented by  $A_{F}$ . Therefore, determining the absorption intensity  $I_{A}(\lambda_{E})$  at 355 nm and  $A_{F} = \int_{375}^{3700} I_{F}(\lambda_{E}, \lambda_{F}, )d\lambda_{F}$  relations between the 4-hydroxyacetophenone and iodinated 4-hydroxyacetophenones, as previous presented in Table 2, the fluorescence quantum yield ratio can be determined by Eq. (4):

$$\frac{\Phi_{Fi}}{\Phi_{Fn}} = \frac{A_{Fi} \cdot I_{An}}{A_{Fn} \cdot I_{Ai}} \tag{4}$$

where the i(n) index represents the iodinated (non-iodinated) molecules. It is important to point out that the k constant possesses the same value for the iodinated and non-iodinated molecules as the same experimental setup was used for obtaining both spectra. The results revealed that  $\Phi_F$  did not change when one iodine atom was introduced into the molecular structure, as presented in Table 3. However, the  $\Phi_F$  of the iodinated molecule containing two iodine atoms was 1.5 higher than the non-iodinated molecule.

In order to check the relationship to the  $\Phi_F$ , the TL characteristic transient signal for the studied samples were determined and fitted by theoretical model proposed by Shen et al. [18]. This model is based in the fact that the probe signal amplitude is proportional to the fraction of the absorbed energy converted into heat ( $\varphi$ ) by the sample, and it is related to the  $\Phi_F$  by the expression  $\varphi = 1 - \Phi_F(\lambda_{exc} < \lambda_{em} >)$ , in which  $<\lambda_{em} >$  is the average emission wavelength. Fig. 3 shows a typical transient signal obtained to the sample #1 diluted at CH<sub>2</sub>Cl<sub>2</sub> solution ( $4.4 \times 10^{-3} \text{ mol L}^{-1}$ ). Similar curves were also obtained to the samples #2 and #3. The open balls are the experimental data and the solid line represents the

Table 3Fluorescence quantum yield obtained by calculating the<br/>absorption and fluorescence intensities.

Sample ratio	$arPsi_F$ ratio
#2/#1 #3/#1	1.00 1.50
	1100
#3/#1	1.50

Table 4

 $\alpha \varphi$ ,  $\varphi$  and  $\Phi$  determined by interpreting the TL experimental results.

Sample ratio	$lpha \varphi$ ratio	$\varphi$ ratio	$\Phi_F$ ratio
#2/#1	1.8	1.0	1.0
#3/#1	1.2	0.4	1.6

theoretical fit curve. It can be noted that after the pump laser is turned on, the central portion of the probe beam in the far field signal is strongly reduced (from 1.00 to ~0.915). This indicates that the heated sample induces a divergence in the probe laser, as expected when solutions are measured by TL technique. Once the pump laser is turned off (at  $t \sim 1.0$  s), the probe laser signal comes back to the initial position, which indicates that the TL effect is reversible and consequently, it does not degrade the sample during the experimental procedure.

According to the fit, the TL characteristic creation time,  $t_c$ , and the phase shift created at the sample,  $\theta$ , due the TL effect, which is proportional to the TL amplitude signal, could be determined. As usual, by using the obtained  $t_c$  value for the 4-hydroxyacetophenone sample diluted at CH<sub>2</sub>Cl<sub>2</sub> ( $t_c = 1.4 \times 10^{-3}$  s) in the relation  $t_c = w_{co}^2/4D$ , together with the value for the excitation beam radius  $w_{oe} = 23.5 \,\mu\text{m}$ , it was possible to calculate the thermal diffusivity (D) for the sample ( $\sim 1.0 \times 10^{-3} \text{ cm}^2/\text{s}$ ). This value is slightly higher than that found by measuring the CH<sub>2</sub>Cl<sub>2</sub> solution without any 4hydroxyacetophenone concentration  $(0.77 \times 10^{-3} \text{ cm}^2/\text{s} \text{ from Ref.})$ [19]), and it was similar to all studied samples. This important fact guarantees that the thermo-optical properties of the studied samples, such as thermal conductivity (K) and temperature dependence of the refractive index (dn/dT) are not affected by the introduction of one or two iodines at 4-hydroxyacetophenone sample. Therefore, by determining the value of  $\theta$  for the studied samples it was possible to calculate the product between the absorption coefficient,  $\alpha$ , and the fraction of the absorbed energy converted into heat by the sample,  $\varphi$ , so  $\theta = (\varphi \alpha)B$  with  $B = (PL/\lambda_pK)$ (dn/dT) and P is the excitation power.

Table 4 shows the obtained results to the product  $\alpha \phi$  for the ratio between sample #2 and sample #1 and also for sample #3 normalized by sample #1. By normalizing the product  $\alpha \varphi$  by the absorbance ratio values exhibit in Table 2, a ratio between  $\phi$  for the samples could be calculate and they are also shown in Table 4. For sample #2/sample #1,  $\varphi = 1$  indicates that the fraction of absorbed energy converted into heat for both samples are identical, suggesting that no difference could be observed in the fluorescence quantum efficiencies for these samples. In opposite way, for the sample #3/sample #1 ratio, it was obtained  $\phi$  = 0.4. This result indicates that there is a strong reduction (60%) in the fraction of absorbed energy converted into heat at the sample #3 when compared to the sample #1. It can be assumed that this reduction in  $\phi$ is an indication that the fluorescence quantum efficiency increases in the same proportion when the two samples are compared. In other words, the thermal lens results are indicating that  $\Phi_{Fi}$  = 1.6  $\Phi_{Fn}$ , which is in good agreement to the values determined above (Table 3) by using the ratio between the fluorescence and absorption data.

#### Conclusions

The molecular absorption studies shown that iodine atoms, as substituent in the aromatic ring, induced a red shift of the absorption bands as well as the emergence of a new band at 242 nm for the 4-hydroxy-3,5-diiodoacetophenone. The results suggest that the red shift was caused by the electron delocalization while the new absorption band at 242 nm was originated by the emergence of a charge transfer band. In addition to the absorption changes, an increase in the fluorescence intensity was also observed for both iodinated acetophenones, the 4-hydroxy-3-iodoacetophenone and the 4-hydroxy-3,5-diiodoacetophenone. However, our results revealed that the  $\Phi_F$  of the 4-hydroxy-3-iodoacetophenone did not change when compared with the 4-hydroxyacetophenone while for the 4-hydroxy-3-iodoacetophenone the  $\Phi_F$  was ~1.55 higher than the non-iodinated molecule. This conclusion was supported by a close analysis of absorption, fluorescence and thermal lens data.

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