

Sulfur aromatic heterocycles: A new kind of solar ultraviolet-B radiation actinometers

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Abstract

Indoline-2-thione (BC) and benzimidazole-2-thione (BN) are two aromatic compounds containing a NCS synthonic unit in a heterocyclic ring of five centres, where the main electronic absorption bands are localized in the spectral range of the ultraviolet A and B.

After ultraviolet irradiation by artificial sources or sunlight, these molecular systems in aqueous solution, under controlled pH, present a simple pattern of photochemical reactions defined by a typical isobestic point in the electronic absorption spectra. The photolysis process observed follows a good linear behavior as function of the irradiation time, being a particular actinometer of short time exposition.

On the other hand, the final photochemical products of indoline-2-thione and benzimidazole-2-thione, after irradiation, were identified as indole and benzimidazole, respectively. Other properties such as molecular stability in acid solution at $\text{pH} < 2$, photochemical conversion in a linear response in the time range from minutes to hours, and photochemical quantum yields are reported.

Due to the use of water as solvent, without a health hazard by direct manipulation, from an environmental point of view we propose these two thione compounds as new potential photochemical actinometers of solar ultraviolet-B radiation.

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1. Introduction

Ultraviolet radiation can be measured from energy conversion electronic devices or from chemical reactions induced by photons. A photochemical system in a physical device by which the number of photons in a beam of radiation can be determined integrally or per time unit is known as an actinometer. Therefore, photochemical products can be directly related to the number of photons absorbed because the chemical action of light induces reversible or irreversible chemical changes to be observed from a decay or build-up of molecules. Thus, an actinometer can be understood as a chemical system that undergoes a light-induced reaction, at a certain wavelength (λ), for which the quantum yield (Φ) is accurately known [1].

Chemical actinometers have advantages in comparison with biological and photoelectronic system for light intensity measurements [2], because do not demand any recalibration and require no specialized equipment. Therefore, photochemical actinometry has been employed increasingly for over 60 years in the radiation area as a relatively simple and accurate method for absolute measurement.

The ferrioxalate actinometer proposed by Parker [3,4] is one of the classical systems commonly used as standard. Though this particular method has universal applicability, it has some disadvantages in its complexity and the necessary analytical procedures are rather time consuming. Alternative liquid phase chemical actinometers have been proposed, where, ideally, the quantum yield for the actinometer reaction should be independent of the reactant concentration, light intensity, temperature and wavelength over a reasonable range. A comprehensive review of chemical actinometry is available [1].

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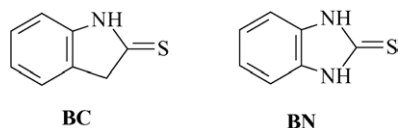


Fig. 1. Indoline-2-thione (BC) and benzimidazole-2-thione (BN).

In this work, we propose two sulfur aromatic heterocycles widely used as bactericides, antipyretics and polymerization accelerators [5,6] as new ultraviolet-B radiation chemical actinometers: indoline-2-thione (BC) and benzimidazole-2-thione (BN) (Fig. 1).

2. Experimental

2.1. Reactants

Indoline-2-thione was synthesized as described in the literature [7–9], by reaction of Lawessons Reagent [10,11] [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide] (7.82 g) with oxindole (3.28 g) in 200 mL of toluene. The final product was characterized by means of ^1H NMR and ^{13}C NMR spectroscopy, ultraviolet absorption electronic spectra and elemental analysis. Benzimidazole-2-thione was purchased from Aldrich Chemical Co. Every compound was re-crystallized and sublimated in a cold finger system prior to preparing fresh aqueous solutions.

2.2. Solutions

The acid aqueous solutions were prepared by dissolving the solid sample in an aqueous solution of H_3PO_4 (1 M). Distilled water and H_3PO_4 (85%, Merck) were used to prepare solutions.

2.3. Spectroscopy

The absorption spectra were recorded in a Perkin-Elmer Lambda 11 UV–vis spectrometer, at room temperature, in a quartz cell of 1 cm length path, while the photolysis of acid solutions was carried out with a high pressure Xenon lamp (300 W).

2.4. Actinometer solution

The absorbed light quanta were estimated using a solution of tris(oxalato)ferrate(III) as actinometer. As recommended by Parker [3], we synthesized and prepared a $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ (6.0 mM) acid solution. For the light intensity determination we prepared a 0.1% of 1,10-phenantroline solution, H_2SO_4 (1N) and a H_2SO_4 (0.36N)–NaAc (0.6N) buffer solution. The irradiation source was a high pressure Xenon lamp (300 W) incorporated in a photon-counting spectrofluorimeter model PC1(ISS), with slits 1.0 and 2.0. The slits were selected in order to achieve

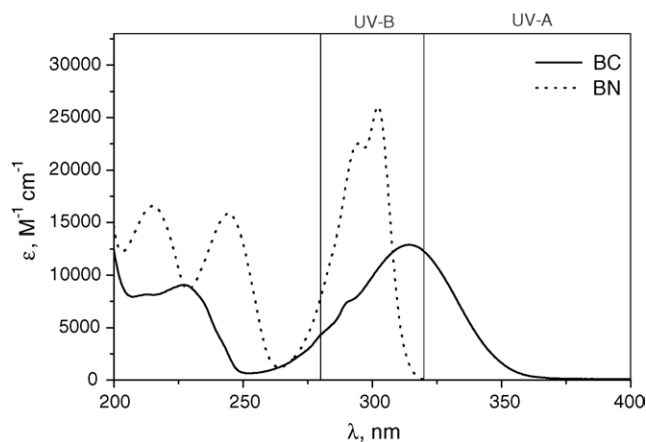


Fig. 2. Absorption spectra of the compounds BC and BN.

high light intensity and minimal bandwidth, with a final value of 8 nm.

3. Results and discussion

Fig. 2 shows the absorption spectra of the compounds BC and BN in acid aqueous solutions, where benzimidazole-2-thione shows an intense $\pi\pi^*$ absorption band in the UV-B region, while indoline-2-thione presents a lower red-shifted absorption band, between the UV-B and UV-A regions.

Fresh BC and BN solutions were prepared before use and the photolysis was carried out under agitation at room temperature, with a high pressure Xe lamp. From Fig. 3, we can see the absorption spectra of the compounds BC and BN, in acid aqueous solution, as a function of the irradiation time. Both compounds present isosbestic points in the whole range of irradiation time. These results determine a singular characteristic in order to consider these compounds as good UV actinometers in acid solution.

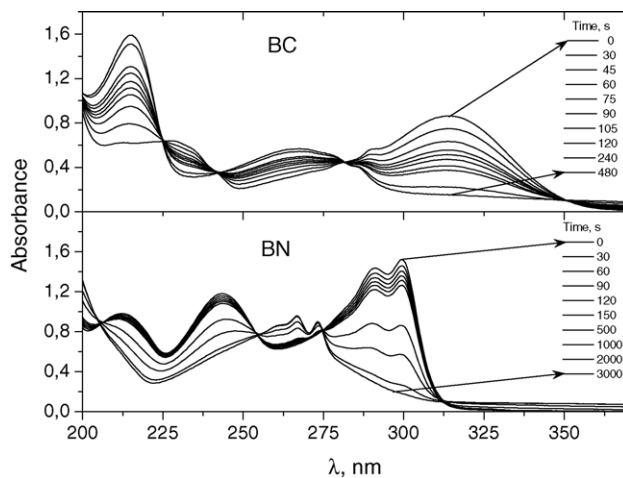


Fig. 3. Absorption spectra of BC and BN as a function of the irradiation time.

The presence of the isosbestic point in Fig. 3 agrees with the direct photodesulfurisation of indoline-2-thione in indole and elemental sulfur, according to our results [7]. In Fig. 4, the absorption spectrum of an irradiated BC acid solution and indole are compared. This result has been corroborated by GC–MS measurements, where the photoproducts obtained after UV-irradiation in acid aqueous solution of H_3PO_4 (1 M in distilled water) determine the main fragment to 117 (m/e), i.e., the main photoproduct corresponds to indole [7]. A similar behaviour is observed by benzimidazole-2-thione, where after UV-irradiation we can observe the benzimidazole as a main photoproduct according to Fig. 4.

The thermal stability of both actinometers in a quartz cell in a dark room, at room temperature, as function of the storage time was studied. In both compounds there is not perceptible change over two days of storage time. On the other hand, a good linear response of the absorbance change as a function of the irradiation time have been observed in the minutes scale, as we see from Fig. 5.

We have determined the photochemical quantum yields of the compound BC for different excitation wavelengths at room temperature as can be seen in Table 1. From these results we can appreciate a constant velocity of the photochemical process as a function of the excitation wavelength, in the 293–334 nm range. We propose a constant quantum yield value of 0.84 ± 0.07 in this wavelength range, with a relative combined standard uncertainty (RCSU) [12] of 9.4%. For BN, we found an average quantum yield value of 0.16 ± 0.01 (RCSU = 7.7%) at 302 nm.

Finally, the actinometers can be easily used from direct detection of the product concentration by UV-absorption measurements in the 293–334 nm range. After prepare a BC or BN solution in water it is necessary to achieve a solute

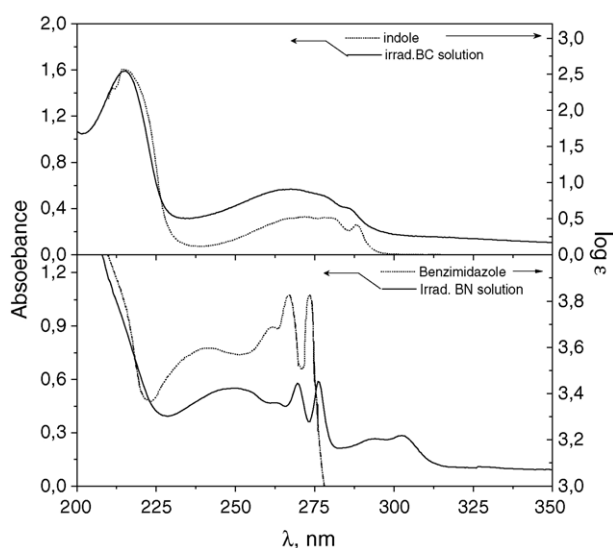


Fig. 4. (Above) Absorption spectra of an irradiated BC solution (—) and indole (···) and (below) absorption spectra of an irradiated BN solution (—) and benzimidazole (···).

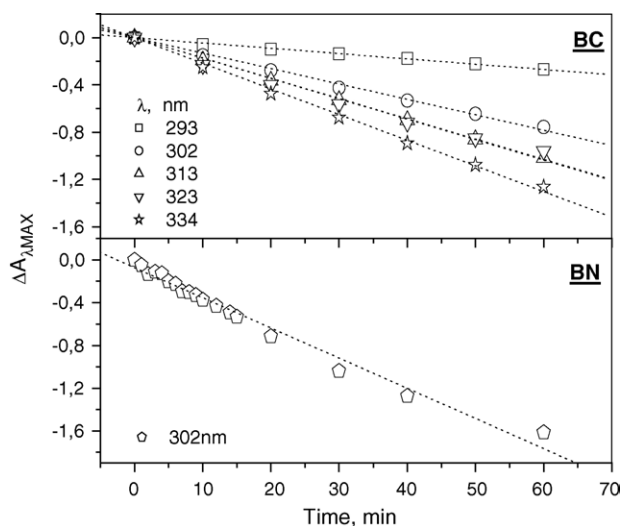


Fig. 5. (Above) ΔA ($\lambda = 336$ nm) for BC as a function of the irradiation time, with a Xe lamp at 293, 302, 313, 323 and 334 nm and (below) ΔA ($\lambda = 300$ nm) for BN as a function of the irradiation time with Xe lamp at 302 nm.

Table 1

Φ_λ as a function of the irradiation wavelength for BC species in acid aqueous solution (pH 1.0)

λ (nm)	Φ_1^a	Error ^b	Φ_2^c	Error ^b	$\langle \Phi_\lambda \rangle^d$
293	0.91	0.01	0.79	0.03	0.85
302	0.86	0.02	0.72	0.02	0.79
313	0.82	0.02	0.84	0.02	0.83
323	0.91	0.03	0.86	0.02	0.88
334	0.89	0.04	0.82	0.01	0.86

^a First determination.

^b Standard deviation for the slope of $n(\text{product})$ vs. $n(\text{photon})$.

^c Second determination.

^d Average of Φ_1 and Φ_2 .

concentration over 2.0 units of absorbance in order to absorb the total UV-radiation.

4. Conclusions

We have found two new UV-actinometers in acid aqueous solution; they are easy to prepare without special safety precautions. On the other hand, these compounds are optically blind to wavelengths above 370 nm, hence an easy manipulation can be made in the laboratory.

The photochemical quantum yields at room temperature present an experimental error of 7.7–9.4 %, which is a precise enough value for these kinds of measurements.

In addition to the use of water as solvent without a health hazard by direct manipulation, from an environmental point of view, we have made use of these actinometers in the UV-B solar radiation measurements. Our results for clean sky solar radiation measurements compare very well to results obtained from *ortho*-nitrobenzaldehyde [13], other broadly used actinometer of short time sun exposition prepared in alcohol solutions.

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