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Photolysis of Some Benzimidazole Based Pesticides

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1. Introduction

The need for increased food production and control of disease vectors brought about a major development in the area of pest control (Martin, H., 1971). Public concern about pesticide contamination only became apparent after the publication of the biologist Rachel Carson (Johnson, D. 1968). This concern has generated a large number of studies in all aspects of pesticide research, including the possible effects and extent of environmental pollution (Tweedy, B. *et al*, 1968; Johnson, D. 1968).

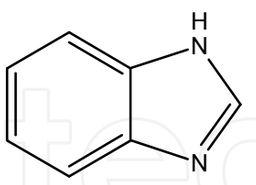
Gaetano Rango… *et al*, studied the photo and thermal degradation of Albendazole, Fenbendazole and Mebendazole. They found that all drugs showed high photosensitivity in solution but a reliable stability in solid form and when exposed to a temperature up to 50 °C. Photolysis was found to cause demethylation or decarboxylation of the parent compounds (Gaetano R., *et al*., 2006).

Abdou M., … *et al*, studied the effect of singlet oxygen on the photostability of Carbendazim in aqueous hydrochloric acid. They could identify some of the photoproducts such as the brownish colored insoluble dimer of benzimidazole (Abdou M. *et al*., 1986). Boudina A. *et al*, investigated the quantum efficiency of carbendazim in aqueous solution and the effect of pH value on the photostability of the pesticide. They suggested a possible phtodegradation mechanism and proposed a final photoproduct using HPLC and GC-MS analytical techniques. Monocarbomethoxy-guanidine was the most stable photoproduct (Boudina A. *et al*., 2003).

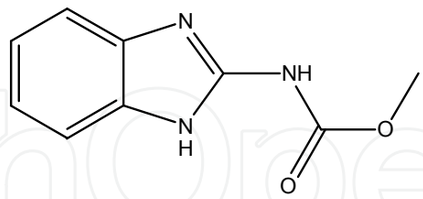
Saien J. and Khezrianjoo studied the kinetic photodegradation of carbendazim in the presence of TiO_2 catalyst (Saien J., and Khezrianjoo S. 2008). Fluorescence quantum yield of Carbendazim in aqueous solution at 254 nm was determined by Mazellier *et al*, (Mazellier P. *et al*. 2002).

The benzimidazole fungicides have been shown to be outstanding agents in disease control (Mazellier P. *et al*. 2002; Fleeker J. and Lacy H., 1977). They are used in the Jordanian agricultural valley where harsh weather conditions are known to exist. Although, such molecules are known to be stable towards solar radiation, the solar spectral distribution in the Jordanian valley extends down to 280 nm where photons in this range of wavelength can be absorbed by such molecules (Yousef A. *et al.,* (2007). Therefore, focusing on the effect of UV light on these molecules can be considered an important agricultural and environmental aspect to that area.

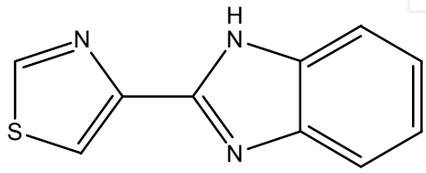
Important members of this group are Methyl 2-Benzimidazolecarbamate [Carbendazime] and 1H-Benzimidazole, 2(-4-thiazolyl) [Thiabendazole]. The molecular structure of benzimidazole and its two derivatives is shown in the figure below,



1H-Benzimidazole



Methyl 2-Benzimidazolecarbamate



1H-Benzimidazole, 2(-4-thiazolyl)

Our interest in the photophysical properties of the benzimidazole analogues arose from earlier work utilizing the photodegradation of Carbaryl and Benomyl in acetonitrile and aqueous solutions (Yousef A. *et al.,* (2007).

In neutral solutions the absorption and fluorescence maxima of benzimidazole and its two derivatives occurs in the UV range between 280 and 350 nm (Boudina A., *et al.*, ; Yousef Y.A, *et al.,* 2001). The main objectives of the project are:

1. To investigate the photodegradation kinetics of above molecules using spectroscopic techniques such as fluorescence and sub nanosecond fluorescence lifetime systems.
2. To characterize the possible photodegradation products using GC/mass spectrometry.

2. Experimental

2.1 Chemicals

Spectroscopic grade acetonitrile purchased from Aldrich Company was used as received. No emission was detected when solvent is excited between (280 –500 nm). Solid samples of benzimidazole, carbendazime and thiabendazole were a gift by a local pesticides production company MOBEDCO. Excitation spectra were used for determining the purity of the fluorescent compounds.

2.2 Instrumentation

Rayonet Photochemical reactor model RPR- 100 manufactured by The Southern New England Ultraviolet Company was used for the photolysis. The unit contains a set of 15 lamps emitting at a maximum wavelength of 300nm. A cooling fan is used to prevent thermal effects on the sample.

Shimadzu Model 1600 was used to record the UV/VIS spectra operating at a medium speed of scanning. All fluorescence measurements were preformed using a home-assembled fluorometer. The system is a modified version of the system mentioned in a previous work (Yousef Y. *et al*, 2007). A block diagram for its different components is shown in figure 1. It is

similar to the previous system except for the air cooled detector model ICCD. The ICCD consists of 512x376 photodide elements with higher sensitivity in the UV region. Fluorescence lifetime measurements were performed using time correlated single photon counting system (TCSPC) from Edinburgh Instruments model- Lifespec-II. Pico-second light emitting diode (LED) light sources and laser diodes were used as the source of excitation. High resolution monochromator of 30cm focal length was used for emission spectral lines separation. The photodetector was a multichannel plate (MCP) with a fast rise time of several picosecends. Special software supplied by Edinburgh Instruments was used for manipulating the decay curves to extract the fluorescence lifetimes.
GC-MS measurements were performed by using a GC model 7100 coupled to VG-7070E E/B sector field mass spectrometer. The system control and acquisition data station, originally supplied with the instrument, was upgraded with new hardware and PC software from MSS Company. The software includes a mass spectral data library from NIST for automatic comparison of sample spectra with a standard. The following conditions were used: Sample volume 3µl, column 10m capillary 0.5mm i.d and 0.25mm stationary phase film thickness, injector temperature 250^{o}C, initial oven temperature 50^{o}C, waiting time 2min, rate 15^{o}C/min, final temperature 300^{o}C, mass range (20- 400 amu), scan rate 15amu/sec, ionization method EI, ion source temperature 250^{o}C, ionization energy 70eV, trap current 50µA. NIST mass data library was used for the identification of the mass spectral results.

3. Results and discussion

3.1 Characterization of fresh samples

The main component in the mobile phase mixture used for the analysis of pesticides by HPLC analytical technique is acetonitrile. Therefore focusing on the photochemical properties and photostability of these molecules in acetonitrile solvent can have important practical applications. The ground state UV absorption spectra of the three pesticides in acetonitrile solvent are shown in figure-1. Benzimidazole absorption spectrum is characterized by two sharp bands at 272 and 280 nm. Carbendazime exhibits two lower resolution and red shifted bands peaking at around 285 and 290 nm. Thiabendazole shows a broad band at around 302 nm with an unresolved tail shoulder at around 315nm. The bands are mainly attributed to n-π^* and π- π^*. Changes in amplitude and position maxima will be used for monitoring the photodegradation of above molecule. A second important technique used to follow the photodegradation is UV fluorescence. Figure-2 shows the emission spectra of the three molecules in acetonitrile solvent. The continuous increase in the width of the emission band and the peak red shift in going from benzimidazole to thiabendazole is clear. Figures 1&2 are used as fingerprints for the molecules in acetonitrile solvent. Knowing the values of absorption and emission of peaks maxima for these molecules are also important for the sensitive detection of molecules by HPLC using UV absorption and fluorescence detection techniques. A complementary technique to fluorescence is fluorescence lifetime. Figure 3, shows the fluorescence decay lifetimes of the molecules in acetonitrile solvent. The decrease in fluorescence lifetime in going from benzimidazole to thiabendazole is clear. Tway et al, were unable to determine the lifetime of benzimidazole due to instrumental limitations (Tway P. C., and Love L. 1992). In this work we report the fluorescence lifetime in acetonitrile solvent to be 5.4 nsec, ± 0.01 nsec. Carbendazim shows a lifetime of 0.7 nsec while thiabendazole has the

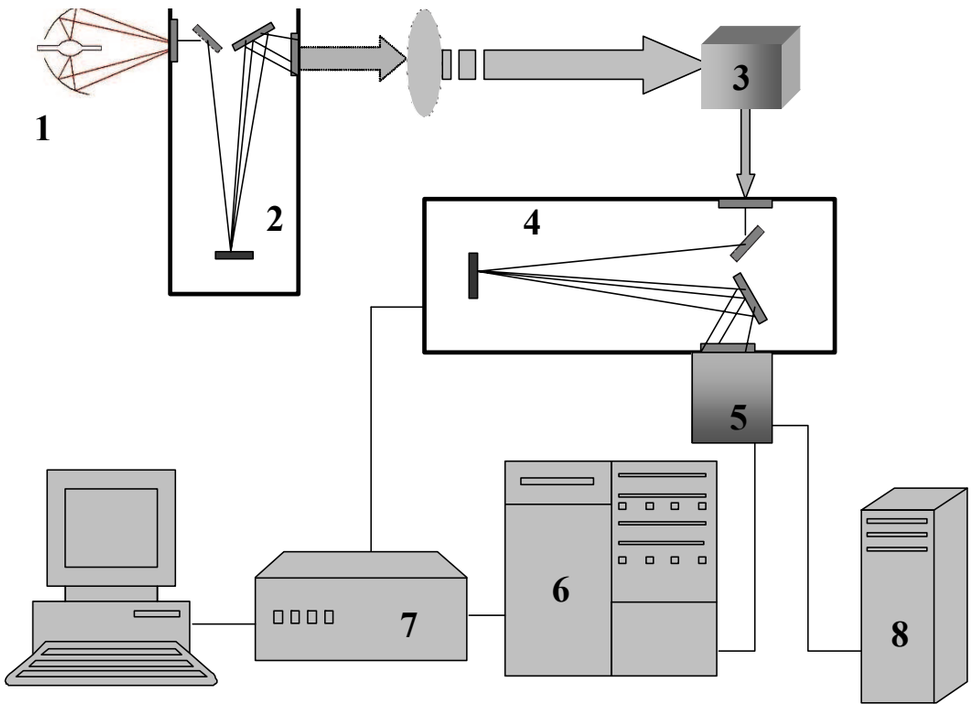


Fig. 1. A block diagram for the home assembled diode array fluorometer. 1- Xe lamp, 2- exc. Monochromator, 3- sample holder, 4- multi-resolution spectrograph, 5- ICCD, 6- detector controller, 7- spectrograph controller, 8- ICCD temperature controller.

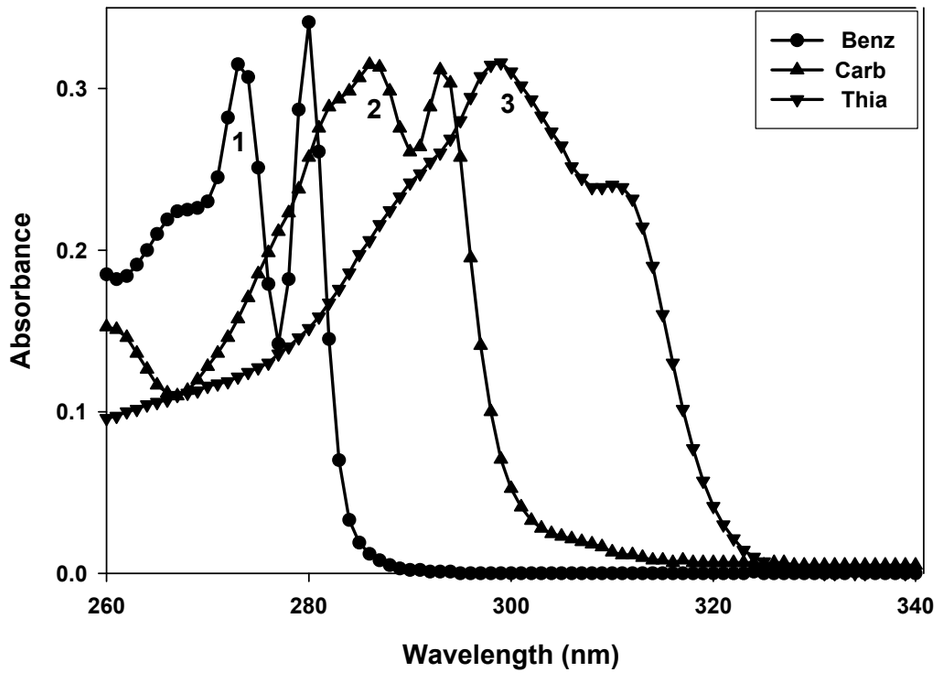


Fig. 2. UV absorption spectra of fresh samples of $1x10^{-4}$M solutions (1) benzimidazole, (2) carbendazime, (3) thiabendazole in acetonitrile solvent.

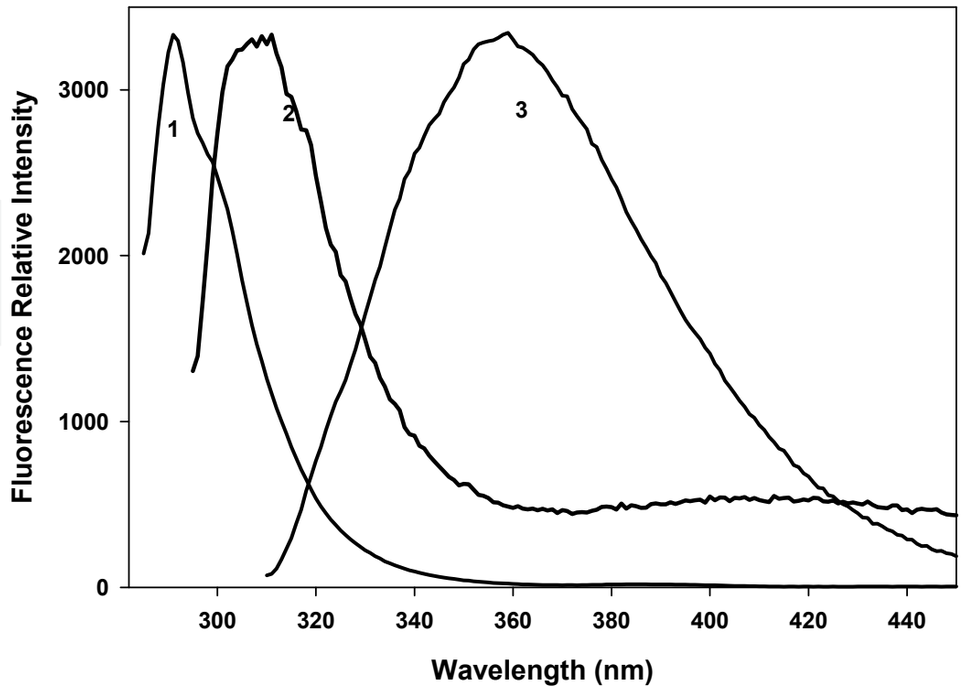


Fig. 3. Fluorescence spectra of fresh samples of $1x10^{-4}$ M solutions (1) benzimidazole, (2) carbendazime, (3) thiabendazole in acetonitrile solvent. Excitation bands correspond to those obtained from the absorption maxima.

shortest lifetime value of 0.3 nsec. Above values correlates well with those obtained by Tway... et al, for carbendazim and thiabedazole pesticides.

Mass spectral analysis of solid and acetonitrile solution samples of the compounds indicated the purity of the compounds. The mass spectrum of each compound was compared with that reported by NIST library data base and found to have exact characteristics. Benzimidazole showed high molecular ion stability. 118 amu was the base peak which corresponds to its molar mass. Carbendazim and thiabendazole showed base peak with a mass lower than the molecular ion peak with values of 191 and 201 amu respectively.

3.2 Photolysis of benzimidazole

Clear changes in the spectra of benzimidazole when UV photolyzed for different periods of time. Figure 4, shows the absorption spectra of fresh and photolyzed samples of benzimidazole in acetonirile solvent. A continuous decrease in the amplitude of the bands at 272 and 280nm accompanied by the appearance of a new broad band between 290 and 400 nm. The appearance of the new band indicates the formation of a new photoproduct. Absorption and fluorescence curve analysis of figures 4and 5, yielded a zero order chemical kinetics for the photodegradation process. Fluorescence lifetime analysis indicated the formation of a photoproduct having a fluorescence lifetime of 1.7 nsec. The decay curve for benzimidazole is of single exponential character where the photolyzed decy curves are of double exponential, as is shown in figure 6. Fluorescence lifetime data for a fresh sample solution of this compound in acetonitrile yielded a value of 1.7 nsec.

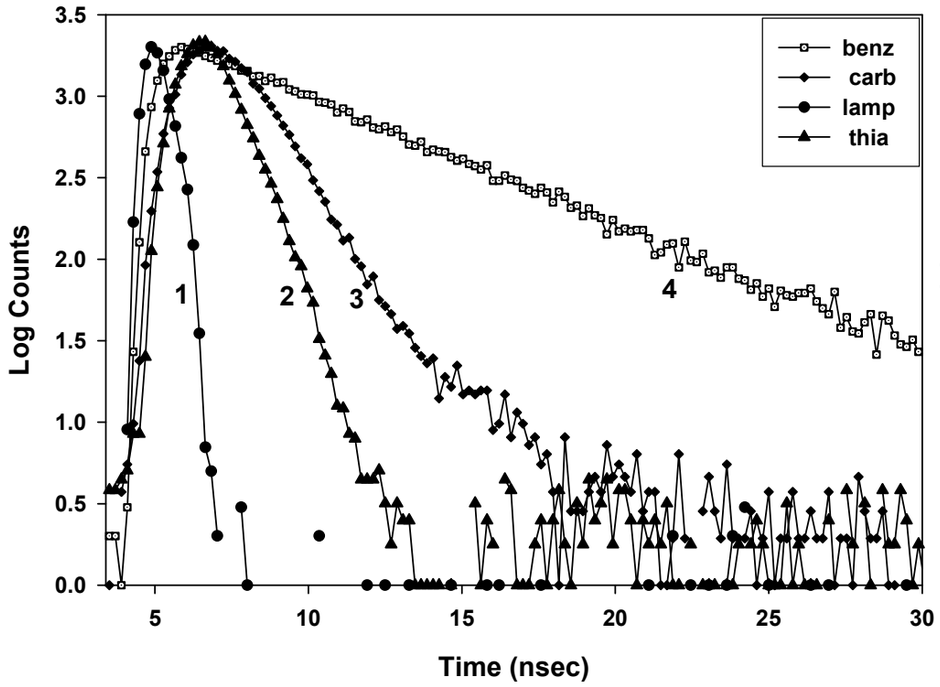


Fig. 4. Decay time curves for a fresh samples of ≈10^{-4} M solutions, (1) lamp pulse decay, (2) thiabendazole, (3) carbendazime, (4) benzimidazole in acetonitrile solvent. Excitation and fluorescence bands correspond to those obtained from the absorption and emission maxima.

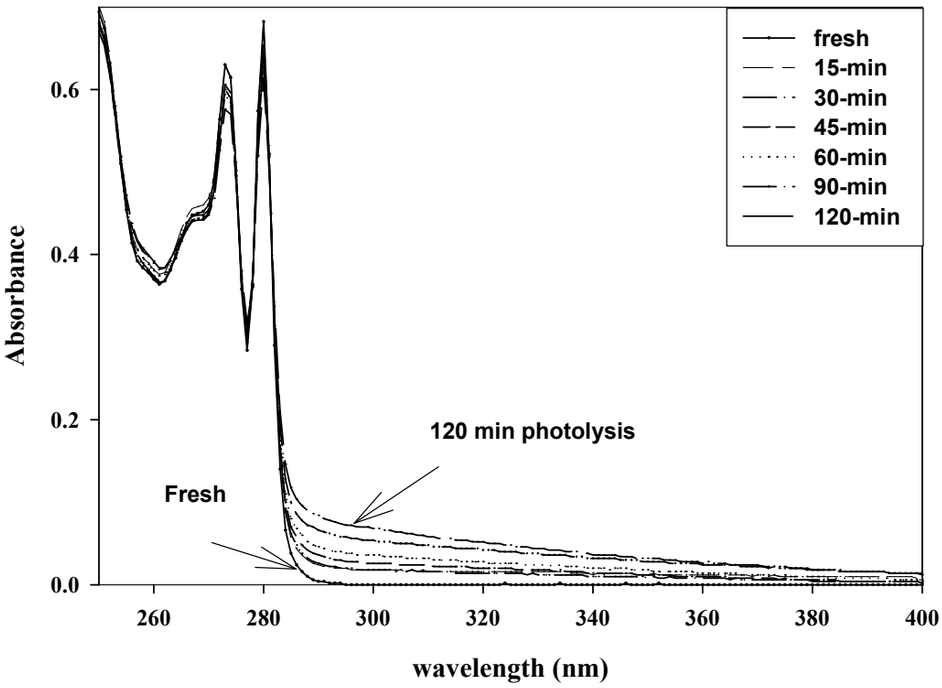


Fig. 5. UV absorption spectra of fresh and photolyzed samples of 1x10^{-4}M solutions of benzimidazole in acetonitrile solvent.

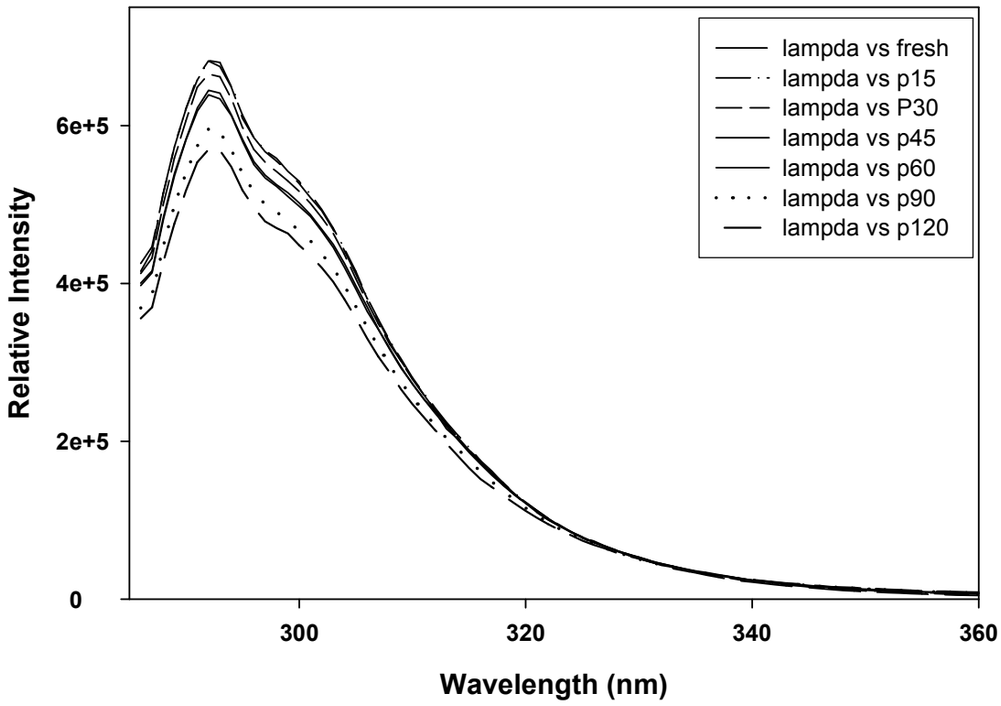


Fig. 6. Fluorescence spectra of fresh and photolyzed samples of $1x10^{-4}$M solutions of benzimidazole in acetonitrile solvent excitated at 280 nm.

GC/MS results reviled the possibility of 2-amino benzimidazole as a possible photoproduct. Mass spectrum was compared with the reported data in the NIST data base. Benzimidazole dimmer was also observed and confirmed by the presence of a molecular ion with an M/z value of 234 amu.

3.3 Photolysis of carbendazime

Photolysis of 2-Benzimidazolecarbamic acid methyl ester (carbendazim) is shown in figures 7, 8 and 9. Photolysis of a fresh sample solution of carbendazim in acetonitrile for 5 minutes caused a large decrease in the absorption maxima specially the band at 290 nm. Further photolysis showed slower changes as is clearly indicated in figure 8. A new and broad band with a maximum around 330 nm is also shown in the figure which indicates the formation of a new photoproduct absorbing in this wavelength range. An isospestic point at around 300 nm is clearly shown in the UV spectra. Normalized fluorescence spectra of fresh and photolized samples of carbendazim solutions are shown in figure 9. The drastic increase in the fluorescence intensity in the range 330 to 400 nm indicates the formation of a photoproduct with a fluorescence maximum at 350 nm. Analysis of the absorption and fluorescence data in figures 8 and 9 reviled a second order kinetics. In comparing the spectra in figures 5and 6 with those in figures 8 and 9 we can conclude that carbendazime have much lower UV photostability than benzimidazole.

Fluorescence decay time results in figure 10, shows decay curves of double exponential nature for photolyzed carbendazim. One exponential corresponds to the parent molecule with a value of about 0.7 nsec, while the second exponential of about 5 nesec indicates the formation of 2-cyanomethyl benzimidazole. Further photolysis showed the degradation of

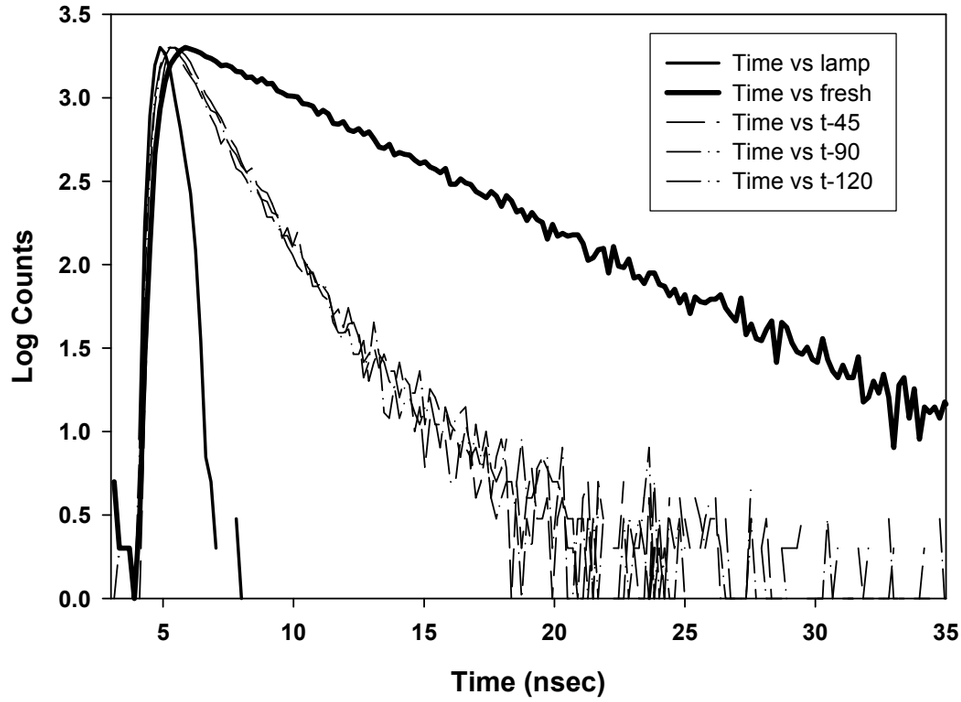


Fig. 7. Fluorescence decay time of fresh and photolyzed samples of $1x10^{-4}$M solutions of benzimidazole in acetonitrile solvent excitated at 280 nm.

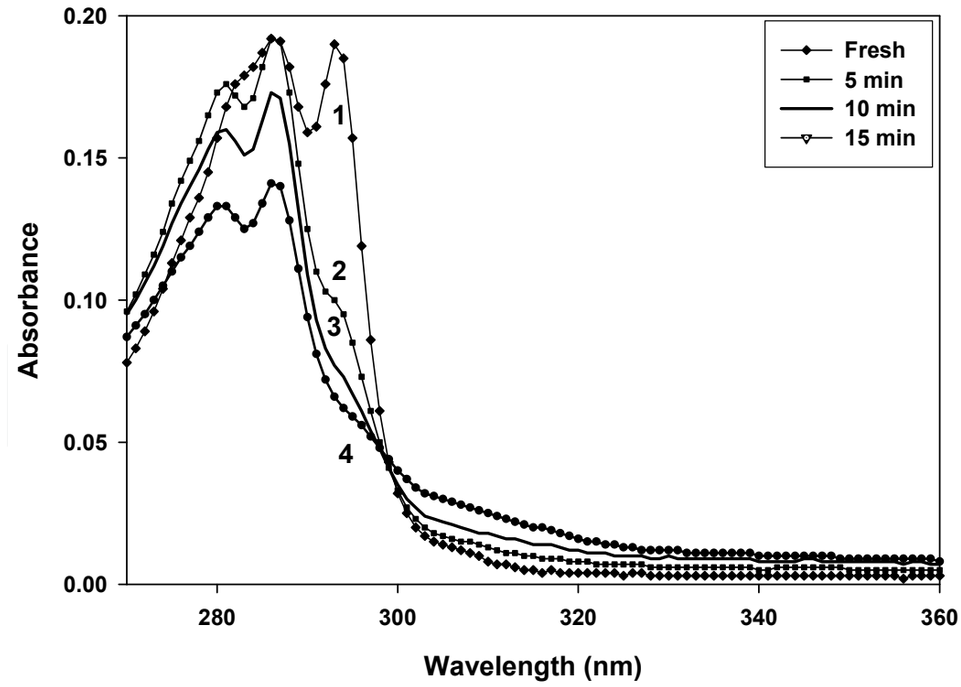


Fig. 8. UV absorption spectra of fresh and photolyzed samples of $0.5x10^{-4}$M solutions of carbendazim in acetonitrile solvent, (1) fresh, (2) 5 min, (3) 10 min, (4) 15 min photolysis periods.

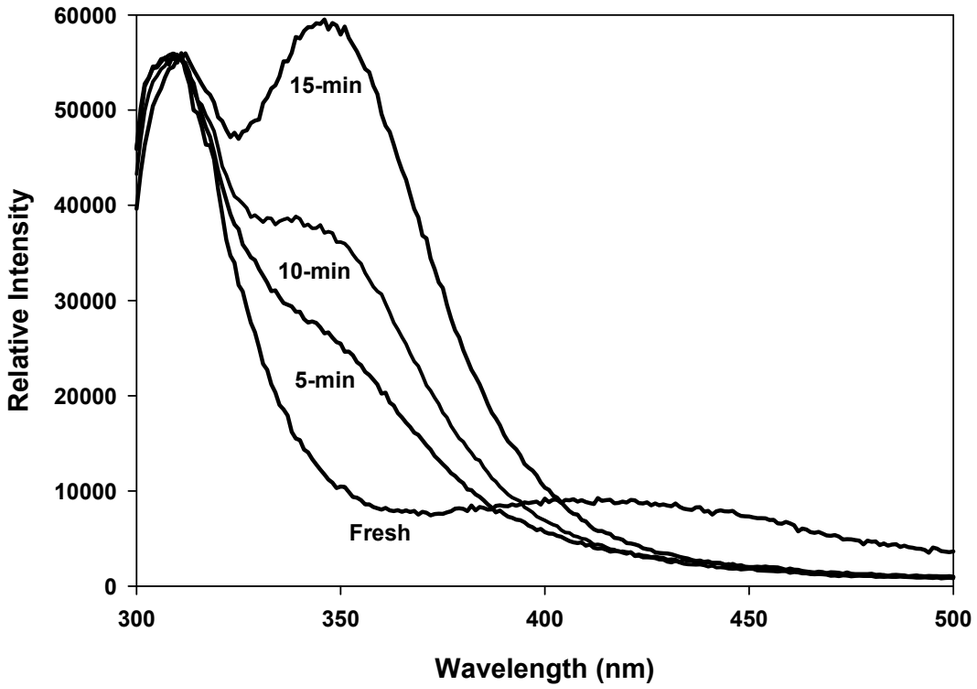


Fig. 9. Normalized fluorescence spectra of fresh and photolyzed samples of $0.5x10^{-4}$ M solutions of carbendazim in acetonitrile solvent excited at 300 nm.

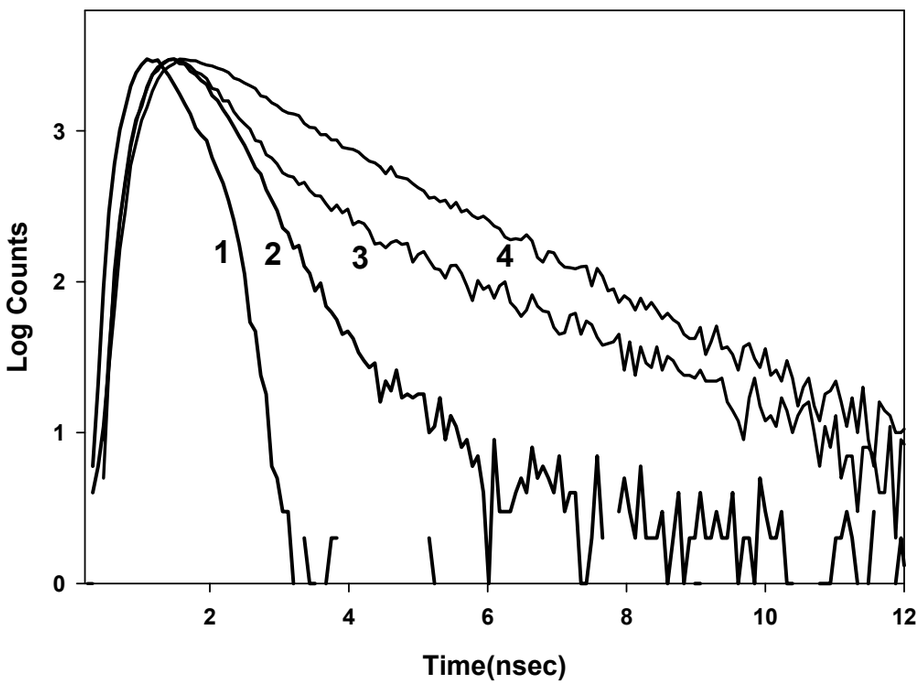


Fig. 10. Fluorescence decay time of fresh and photolyzed samples of $0.5x10^{-4}$ M solutions of carbendazim in acetonitrile solvent excited at 300 nm. (1) lamp, (2) Fresh, (3) 10 min, (4) 20 min photolysis time.

the primary potoproduct to those obtained by benzimidaole with a lifetime of about 1.7 nsec. Fluorescence lifetime technique proved to be a powerful system for monitoring photodegradation process. GC/MS analysis supported the above results obtained by the presence of a molecular ion with am M/z of 157amu during the first periods of photolysis.

3.4 Photolysis of thiabendazole

Benzimidazole 2- (4-thiazolyl) commonly named thiabendazole was irradiated for different periods of time. Photodegradation was monitored by UV absorption, fluorescence, and lifetime spectroscopic techniques. Thiabendazole shoed high sensitivity to UV radiation as is clearly appears in figures 11, 12 and 13. Figure 11 shows the absorption spectra for fresh and photolyzed sample solutions in acetonitrle. The band at 295nm almost disappeared within the first 5 minutes of irradiation. The new band between 300 and 350 nm characterize the new photoproduct. An isospestic point around 300 nm is clearly shown in the figure. Analysis for the data in figure 11 confirmed that photodegradation follows 2nd order kinetics. Emission spectra for fresh and photolyzed samples of the molecule for different irradiation periods. Continuous decrease in fluorescence intensity at around 360 nm accompanied by the formation of a new and increasing band at around 450 nm can noticed. An isospestic point at about 420 nm is shown. Data analysis indicated that photodegradation follows 2nd order kinetics. Fluorescence lifetime data in figure 13 can be used to follow the photodegradation at the end of each irradiation period. Fresh sample gave a short lifetime of 0.2 nsec. Photolysis resulted in the formation of a photoproduct with fluorescence lifetime of 5 nsec corresponding to the formation of benzimidazole as a photoproduct. GC/MS spectral analysis showed the appearance of a mass at 118 amu which is the mass of benzimidazole.

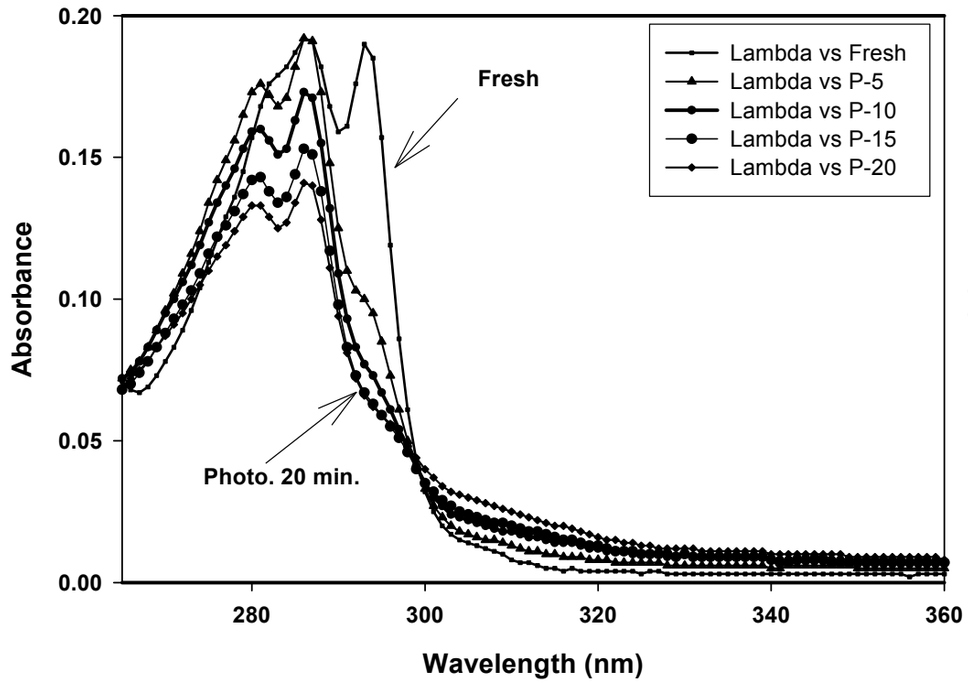


Fig. 11. UV absorption spectra of fresh and photolyzed samples of 1.5x10-4M solutions of thiabendazole in acetonitrile solvent.

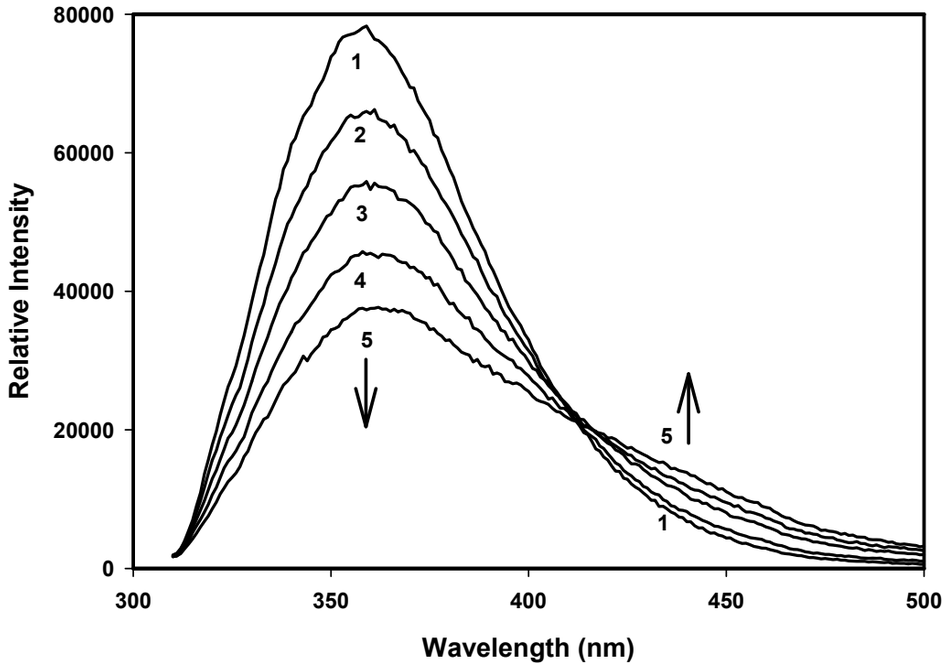


Fig. 12. Fluorescence spectra of fresh and photolyzed samples of $1.5x10^{-4}$M solutions of thiabendazole in acetonitrile solvent excited at 300 nm. (1) fresh, 2 5 min, (3) 10 min, (4) 15 min, (5) 20 min photolysis periods

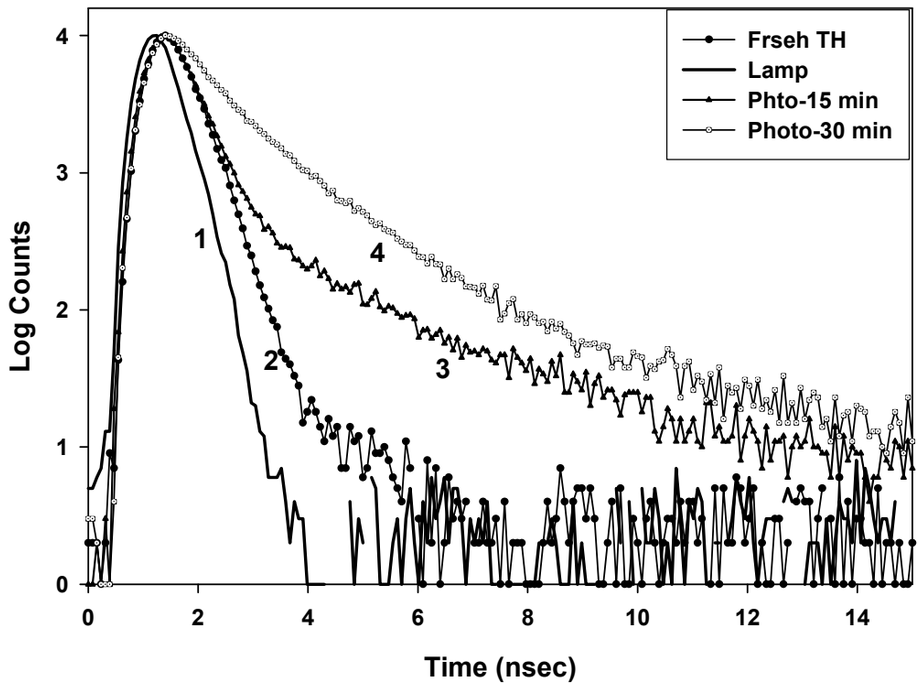


Fig. 13. Fluoresence decay time of fresh and photolyzed samples of $1.5x10^{-4}$M solutions of thiabendazole in acetonitrile solvent excited at 300 nm. (1) lamp, (2) Fresh, (3) 10 min, (4) 20 min photolysis time.

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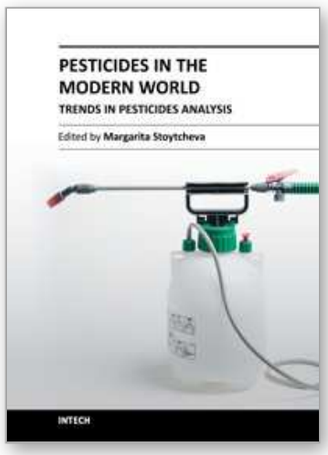

Pesticides in the Modern World - Trends in Pesticides Analysis
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The book offers a professional look on the recent achievements and emerging trends in pesticides analysis, including pesticides identification and characterization. The 20 chapters are organized in three sections. The first book section addresses issues associated with pesticides classification, pesticides properties and environmental risks, and pesticides safe management, and provides a general overview on the advanced chromatographic and sensors- and biosensors-based methods for pesticides determination. The second book section is specially devoted to the chromatographic pesticides quantification, including sample preparation. The basic principles of the modern extraction techniques, such as: accelerated solvent extraction, supercritical fluid extraction, microwave assisted extraction, solid phase extraction, solid phase microextraction, matrix solid phase dispersion extraction, cloud point extraction, and QuEChERS are comprehensively described and critically evaluated. The third book section describes some alternative analytical approaches to the conventional methods of pesticides determination. These include voltammetric techniques making use of electrochemical sensors and biosensors, and solid-phase spectrometry combined with flow-injection analysis applying flow-based optosensors.

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