Spectrochimica Acta Part A 78 (2011) 1027–1036

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Synthesis, structure investigation, spectral characteristics and biological activities of some novel azodyes

M.A. Zayed [a,*], Gehad G. Mohamed [a], S.A.M. Abdullah [b]

[a] Chemistry Department, Faculty of Science, Cairo University, 12613 Giza, Egypt
[b] University of Workers,10 Aswan, Egypt

ARTICLE INFO

Article history:
Received 17 September 2010
Received in revised form
25 November 2010
Accepted 10 December 2010

Keywords:
Acetoamidophenolazo compounds
UV–vis
FT-IR
^{1}H NMR
Mass spectra
MO calculations
Biological activity

ABSTRACT

Four novel azo compounds were synthesized; o-phenylazo- ($C_{14}H_{13}N_3O_2$) (I), p-bromo-o-phenylazo- ($C_{14}H_{13}BrN_3O_2$) (II), p-methoxy-o-phenaylazo- ($C_{15}H_{16}N_3O_3$) (III) and p-nitro-o-phenylazo-p-acetamidophenol ($C_{14}H_{13}N_4O_4$) (IV). These compounds were carefully investigated using elemental analyses, UV–vis, FT-IR, ^{1}H NMR and mass spectra. Also, the effects of p-substituents such as bromo, methoxy and nitro groups on the mass fragmentation pathways of these dyes were studied using Hammet's effects. This research aimed chiefly to threw lights on the structures–stability relationship of four novel newly prepared azo derivatives of p-acetoamidophenol. The data obtained referred to the variation of mass fragmentation pathways with the variation of p-substituent of these dyes which can be used in industry for various dyeing purposes. This variation is also correlated and verified by molecular orbital calculations which were done on ionic forms of these dyes using semi empirical PM3 program. The biological activities of these dyes were also investigated and its structure relationship was correlated.

1. Introduction

Recently, several studies have been published on the synthesis and spectral properties of azo dyes [1–3]. This reflects their widely important applications in different fields, such as polyester fiber [4] and disperses dyes [5], as well as their involvement in many biological reactions and in analytical chemistry [6].

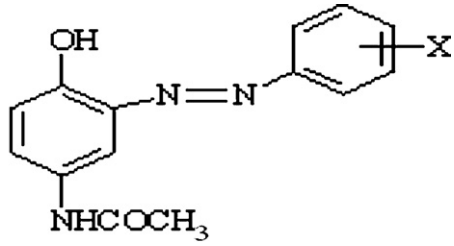
Photochromic compounds are receiving more interest due to their potential applications in photonic devices such as optical memories, photo-switches, and full color displays [7–9]. The photochromic properties of the some dyes depend on several factors, such as the nature of the heteroaryl moieties, the conformation of the open-ring isomer, electron donor/acceptor substituents, and the p-conjugation length of the hetero-aryl groups, among others [10]. Electron-donating substituents can increase the absorption coefficients and decrease the cycloreversion quantum yields of some dyes, while electron-withdrawing groups do not affect the cycloreversion quantum yield but can shift the absorption maxima to longer wavelengths [11]. The longer the p-conjugation length of the hetero-aryl groups, the lower the cycloreversion quantum yields of diarylethenes [12,13]. The potential of organic dyes and their intermediates to adversely impact human health and the environment has moved toxicological considerations to the forefront of their molecular design [14].

Mass spectrometry plays pivotal role in the structural characterization of organic molecules [15]. In conjunction with mass spectrometric analysis [16,17], computational quantum chemistry can provide additional information about the atoms and bonds, which can be used successfully in an interpretation of experimental results [18].

The aim of the present work is to carry out experimental and theoretical investigation of the four azo compounds of the biological activity of p-acetamidophenol using UV–vis, FT-IR, ^{1}H NMR and EI mass spectral (MS) fragmentation at 70 eV. Also, MO calculations are performed using PM3 procedure, on the charged molecular ion to investigate bond length, bond order, heats of formation, ionization energy and charge distribution. These calculations are correlated with the EI-MS experimental results to obtain information about the stability of the studied compounds and prediction of the site of primary fragmentation step and subsequent ones. Also, it is used to discuss the effect of Hammet values of substituents on experimental and computational results. The biological activities of the azodyes under investigation are reported using *Tribolium confusum*. The structures of the azodyes (I–IV) are given in Fig. 1.

* Corresponding author. Tel.: +20 105776675; fax: +2 002 35728843/7556.
E-mail address: mazayed429@yahoo.com (M.A. Zayed).

1386-1425/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2010.12.037



I, X = H
II, X = p-Br
III, X = p-OCH_3
IV, X = p-NO_2

Fig. 1. Structure of azodyes (I–IV).

2. Experimental

2.1. Reagents

All the chemicals used in this work were of analytical grade. They included p-acetamidophenol, aniline, p-bromoaniline, p-methoxyaniline, and p-nitroaniline (Sigma) sodium nitrite and sodium hydroxide (Adwik). Organic solvents (spectroscopic pure from BDH) used included absolute ethyl alcohol, diethylether and dichloromethane.

2.2. Preparation of dyes (I–IV)

p-Acetamidophenol-azo-derivatives (I–IV) were prepared by coupling p-acetamidophenol with aryl, p-bromo-, p-methoxy- and p-nitro-diazonium chloride, in an ice bath, in the presence of sodium hydroxide [19]. The precipitates were left in refrigerator over night, filtered and crystallized from acetic acid (yield 78–86%).

2.3. Solutions

The solutions used in UV–vis. measurements are obtained by dissolving the accurate weight of the corresponding dye in ethanol or in methylene chloride. The concentrations of the studied dyes are 0.1574×10^{-3} M, 0.126×10^{-3} M, 0.143×10^{-3} M and 0.137×10^{-2} M for dyes I, II, III and IV, respectively.

2.4. Instruments

Elemental microanalyses of the separated solid dyes for C, H and N were performed at the Microanalytical Center, Cairo University, using CHNS-932 (LECO) Vario Elemental Analyzers. The UV–vis electronic spectra of dyes (I–IV) were measured in methanol and in methylene chloride (MC) solvents using Shimadzu recording spectrophotometer UV/VIS/NIR 3101 PC model in the region of λ = 200–800 nm. The infrared spectra were recorded on a PerkinElmer FT-IR type 1650 spectrophotometer in wave number region 4000–400 cm^{-1}. The spectra were recorded as KBr pellets. ^{1}H NMR spectra were measured using an instrument of Model Gemini 2000 Switzerland using duterated dimethylsulphoxide (DMSO-d_6) and measured in Micro Analytical Center, Cairo University. Electron ionization mass spectra (EI-MS) of the studied dyes were obtained using Shimadzu GC-MS-Qp 1000 PX quadruple mass spectrometer with electron multiplier detector equipped with GC–MS data system. The direct probe (DP) for solid material was used in this study. The EI-MS spectra were obtained at ionizing energy value of 70 eV, ionization current of 60 μA and vacuum is better that 10^{-6} Torr.

The molecular orbital calculations (MOCs) were performed using semi-empirical molecular orbital calculation. The method used in these computations is the parametric method (PM3) described by Stewart [20]. The default criteria for terminating all optimizations were increased by a factor of 100 (keyword PRECISE). Vibrational frequencies were computed for the studied structures (keyword FORCE) so as to check whether the newly designed geometries are local minima. All the molecular orbital calculations were carried out at the unrestricted Hartree–Fock level (UHF) for there positively charged ions using PM-3 method followed by full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles), without any symmetry constraint. All structures were optimized to a gradient normalization of 0.01–0.05, using the eigenvector following (EF) routine [21]. All the semi empirical MO calculations were performed with the MOPAC2000 software package [22] implemented on an Intel Pentium IV 3.0 G Hz computer.

2.5. Biological activity

Adult of *T. confusum* were laboratory reared on wheat flour at 27.5 ± 1.5 °C and 70% ± 5% (R.H.) according to the method of Frederic et al. [23] with some modifications.

T. confusum adult was topically treated with 10 μm of each compound according to the protocol described by Delobel et al. [24] as follows: thirty insects divided on three replicates (10 adult/replicate) were topically and mortality was then monitored after 24 h. Thirty adults of control experiment were used in three replicates without treatment. The adult mortality was estimated according to Abbot Method [25]. Estimation of LD50 values was made using probity analysis as given by Finney [26].

3. Results and discussion

The structure elucidation of the prepared azodyes (I–IV) is carried out by using different techniques namely elemental analyses, UV–vis, FT-IR and ^{1}H NMR and mass spectroscopy, in addition to molecular orbital calculations.

The elemental analyses of the prepared dyes referred to the general formulae of o-phenylazo- ($C_{14}H_{13}N_3O_2$) (I), p-bromo-o-phenylazo- ($C_{14}H_{13}BrN_3O_2$) (II), p-methoxy-o-phenaylazo- ($C_{15}H_{16}N_3O_3$) (III) and p-nitro-o-phenylazo-p-acetamidophenol ($C_{14}H_{13}N_4O_4$) (IV) compounds, respectively.

3.1. UV–vis absorption spectra

These structures are confirmed by the UV–visible spectra in ethanol (Fig. 2a) and in methylene chloride (Fig. 2b). The correlation between the structural formulae of these dyes and the absorption spectral data is given in Table 1. The electronic transition n–π* ($\varepsilon \approx 10^3$ L mol^{-1} cm^{-1}, $\lambda_{max} \approx 330$–439 nm) generally occurs in amide carbonyl in dyes I–III together with that occurs in NO_2 group in dye IV and π–π* electronic transition ($\varepsilon \approx 10^4$ L mol^{-1} cm^{-1}, $\lambda_{max} \approx 230$–260 nm) occurs in azo group/and or other unsaturated bonds in all dyes (I–IV). These transitions in ethanol are of less molar absorptivity than in methylene chloride for all dyes. This is may be attributed to the effect of polarity difference of the two solvents. The position of their bands (Fig. 2) is varied from one dye to the other and from one solvent to another which may be attributed to the p-phenylazo substituent variable donating power.