Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 106 (2013) 12–18

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Synthesis, structure characterization and antimicrobial evaluation of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles

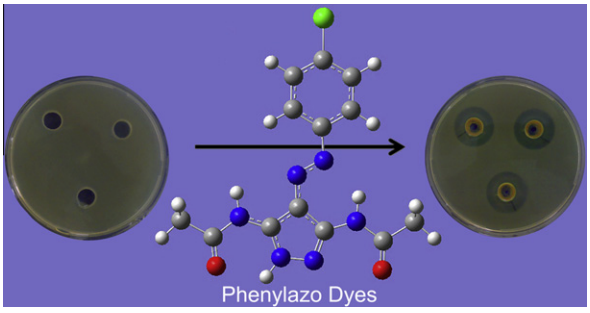
Selin Kinali-Demirci [a], Serkan Demirci [b,*], Mustafa Kurt [c]

[a] Department of Chemistry, Faculty of Science, Gazi University, 06500 Ankara, Turkey
[b] Department of Chemistry, Faculty of Arts and Sciences, Amasya University, 05100 Amasya, Turkey
[c] Department of Physics, Faculty of Arts and Sciences, Ahi Evran University, 40100 Kırsehir, Turkey

HIGHLIGHTS

- 4-(Substituted phenylazo)-3,5-diacetamido-1H-pyrazoles were synthesized.
- Phenylazo dyes were examined by FT-IR, FT-Raman, UV, NMR techniques and DFT.
- Phenylazo dyes were screened for their antibacterial and antifungal activity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 October 2012
Received in revised form 17 December 2012
Accepted 22 December 2012
Available online 4 January 2013

Keywords:
Phenylazo dyes
Solvatochromism
Vibrational spectra
DFT
Antimicrobial activity

ABSTRACT

The present article deals with the synthesis, spectral characterization and antimicrobial activity of phenylazo dyes. All of the synthesized phenylazo dyes were characterized using ATR-FTIR, FT-Raman, ^{1}H NMR, ^{13}C NMR, elemental analysis and mass spectroscopic techniques. Solvent effects on the UV–Vis absorption spectra of these phenylazo dyes were studied. Acid and base effects on the visible absorption maxima of the phenylazo dyes were also reported. The structural and spectroscopic analysis of the molecules were carried out using Density Functional Theory (DFT) employing the standard 6-31G(d) basis set, and the optimized geometries and calculated vibrational frequencies were evaluated via comparison with experimental values. The antimicrobial activity of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles was reported against bacteria, including *B. cereus* (RSKK 863), *S. aureus* (ATCC 259231), *M. luteus* (NRRL B-4375), *E. coli* (ATCC 11230) and the yeast *C. albicans* (ATCC 10239).

Introduction

Azo compounds are the largest class of industrially synthesized organic dyes and are important materials because of their versatile applications in various fields, such as electronics, foods, drugs, cosmetics and textiles [1–5]. Several studies describe the synthesis [6–9], absorption spectra [10,11], solvatochromic behavior [12,13] and theoretical investigation [14–16] of azo dyes. Azo dyes contain at least one nitrogen–nitrogen double bond called azo group (N=N) [17,18]. Azo groups are relatively robust and chemically stable, and therefore, extensive studies have been carried out investigating azobenzene based structures as dyes and colorants. The aromatic groups around the azo bond help to stabilize the N=N group by making it part of an extended delocalized system. The synthesis, chemical structure and methods of application for these compounds are generally not complex.

Tautomerism is not only important to the dyestuff manufacturer, but it is also important in other areas of chemistry. Specifically, the azo-hydrazone tautomerism is quite interesting for theoretical studies and is also important from a practical

* Corresponding author. Tel.: +90 358 242 1613; fax: +90 358 242 1616.
E-mail addresses: srkndemirci@gmail.com, serkan.demirci@amasya.edu.tr (S. Demirci).

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2012.12.074

perspective because the two tautomers have different properties [14]. Although many commercially available azo dyes are predominantly in the hydrazone form [19], in light-sensitive studies, including polymer [20–22] and controlled release [23], the azo form of the dye is preferred.

Although, the synthesis of 4-(4-substituted phenylazo)-3,5-diacetamido-1H-pyrazoles has been reported by Elnagdi et al. [24], to our knowledge, the antimicrobial activity, electronic spectra and molecular structure of these dyes have not been studied. In this paper, we present the synthesis of new phenylazo dyes. The antimicrobial activity and absorption ability of these dyes that are substituted with different groups at their *o*-, *m*- and *p*-position were also examined in detail. The calculated vibrational wavenumbers and chemical shifts were compared with the experimental data for the mentioned molecules.

Experimental

Synthesis of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles

The synthesis of 2-(substituted phenylazo)malononitriles and 4-(substituted phenylazo)-3,5-diamino-1H-pyrazoles was carried out according to the methods in the literature [24]. Equimolar amounts of 4-(substituted phenylazo)-3,5-diamino-1H-pyrazoles and acetic acid were refluxed for 24 h [24]. After the reaction was complete, the reaction mixture was chilled in an ice bath. The precipitated product was filtered off and recrystallized from an appropriate solvent. The crystalline product was dried overnight under a vacuum at room temperature (Scheme 1). The appearance, yield, crystallization solvent, melting point and elemental analysis of the phenylazo dyes are given in Table 1.

Computational details

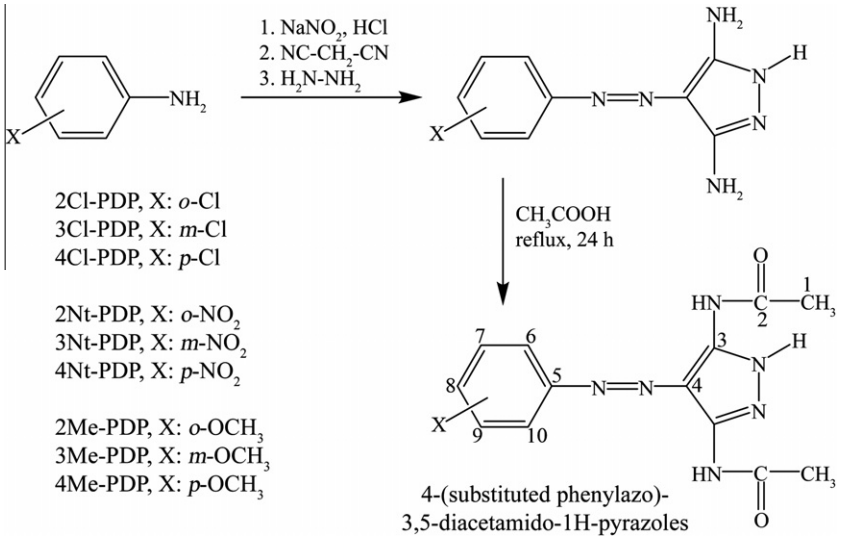
Calculations for the electronic structure and geometry optimization of the phenylazo dyes were performed using the Gaussian 09 program [25] package and the Gauss-View molecular visualization program [26]. The molecular structures of the phenylazo dyes were optimized using the DFT/B3LYP level with the 6-31G(d) basis set [27]. The optimized structural parameters were used in the vibrational wavenumbers. The stability of the optimized geometries was confirmed by vibrational spectra calculations, which gave positive values for all of the obtained wavenumbers.

Antimicrobial activity of phenylazo dyes

The *in vitro* antibacterial activities of the phenylazo dyes were studied using the agar well-diffusion method in the bactericidal and fungicidal testing. The origin of the microbial strains are *B. cereus* RSKK 863, *S. aureus* ATCC 259231, *M. luteus* NRLL B-4375, *E. coli* ATCC 11230 and *C. albicans* ATCC 10239 as yeast. The bacterial and yeast cultures were incubated at 37 °C for 18 h. The phenylazo dyes were dissolved (20 μg/mL) in DMSO and stored at room temperature. Mueller Hinton Agar (15 mL) that was stored at ca. 45 °C was then poured into the petri dishes and allowed to solidify. Holes of 12 mm in diameter were punched carefully using a sterile cork borer, and these were completely filled with the test solutions. The plates were incubated for 24 h at 37 °C. The mean value obtained for the two holes was used to calculate the zone of growth inhibition for each sample. DMSO was used by itself as a control under the same conditions for the tested microorganisms. The diameter of the inhibition zone resulting from DMSO was subtracted from each case. The antimicrobial activity results were calculated as the mean of three trials.

Physical measurements

The melting points were determined on a Barnstead Electrothermal 9200 melting point instrument. Mass spectra were taken on an Agilent 1100 MSD instrument. The elemental analyses (C, H and N) were performed on a Leco CHNS-932 type elemental analyzer. Fourier Transform Infrared (ATR-FTIR) spectra of the 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles were obtained using a Thermo Nicolet 6700 spectrometer with a Smart Orbit attenuated total reflection attachment. The FT-Raman spectra of the samples were recorded in the 50–3500 cm^{-1} region on a Bruker FRA 106/S FT-Raman instrument using 1064 nm excitation from an Nd:YAG laser. The detector is a liquid nitrogen cooled Ge detector. NMR spectra were recorded on a Bruker-Spectrospin Avance DPX 400 Ultra-Shield NMR spectrometer with chemical shifts in ppm (for $CDCl_3$, tetramethylsilane was used an as internal standard). The absorption spectra were measured on a Unicam UV2-100 spectrophotometer at the wavelength of maximum



Scheme 1. Synthesis of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles.

Table 1
The appearance, yield, crystallisation solvent, melting point and elemental analysis of phenylazo dyes.

Dye	Appearance	Yield (%)	Crystallization solvent	Melting point (°C)	Molecular formula (mol. wt)	C% calc. (exp.)	H% calc. (exp.)	N% calc. (exp.)
2Cl-PDP	Brown	57	Toluene	292–293	$C_{13}H_{13}ClN_6O_2$ (320.7)	48.68 (48.65)	4.08 (4.04)	26.20 (26.22)
3Cl-PDP	Yellow	75	Ethanol/H_2O	235–237				
4Cl-PDP[a]	Dark yellow	58	Ethanol/H_2O	276–278				
2Nt-PDP	Orange	82	Toluene	220–221	$C_{13}H_{13}N_7O_4$ (331.3)	47.13 (47.08)	3.95 (3.89)	29.60 (29.55)
3Nt-PDP	Brown	97	Ethanol/H_2O	244–246				
4Nt-PDP[a]	Brown	52	Toluene	211–213				
2Me-PDP	Yellow	55	Toluene	238–239	$C_{14}H_{16}N_6O_3$ (316.3)	53.16 (53.10)	5.10 (5.02)	26.57 (26.49)
3Me-PDP	Yellow	73	Toluene	217–219				
4Me-PDP[a]	Red	97	Toluene	183–185				

[a] Literature [24].

absorption (λ_{max}) in a range of solvents, including DMSO, DMF, methanol, acetonitrile, acetic acid and chloroform, at various concentrations (10^{-6}–10^{-8}).

Results and discussion

Vibrational analysis

The structures of the phenylazo dyes were elucidated using spectroscopic methods. The experimental ATR-FTIR spectral data for the dyes are shown in Fig. 1. The experimental ATR-FTIR spectra of the phenylazo dyes showed a band at 3450–3200 cm^{-1}, which was assigned to the —N—H stretching. The C═O stretching bands of the dyes are located at 1700–1680 cm^{-1} in all of the experimental spectra for the phenylazo dyes. The theoretical wavenumbers for the phenylazo dyes were calculated using the density functional B3LYP/6-31G(d) method with a scaling factor of 0.9613 [27], and the selected wavenumbers are summarized in Table S1 (Supplementary information). The calculated wavenumbers for the —N—H and C═O stretching are shown at 3500–3300 cm^{-1} and 1750–1700 cm^{-1}, respectively. There were 10–50 cm^{-1} shifts to lower wavenumbers observed for the N—H and C═O stretching bands of the experimental ATR-FTIR spectra compared with the theoretical FTIR spectra. This observation strongly supports the idea that a hydrogen bond can form between the —N—H and C═O groups. The characteristic band (N═N) of the phenylazo dyes appeared at 1400 cm^{-1} in the theoretical FTIR spectra. However, in the experimental FTIR spectra of the dyes, the N═N stretching shifted to a lower wavenumber (1390–1370 cm^{-1}) and depended on the neighbouring group and intermolecular hydrogen bonding. Similarly, the azo stretching of the phenylazo dyes shifted to lower wavenumbers in the experimental Raman spectra (Fig. 2).

The experimental chemical shifts of phenylazo dyes are presented in Table S2 (Supplementary information). Two broad peak approximately 11.0 and 9.0 ppm are assigned to N-H proton. The multiplet between 7.9 and 7.1 ppm are assigned to aromatic ring protons [28,29], and the singlet approximately 2.3 ppm are assigned to acetate (—$COCH_3$) protons for all of the phenylazo dyes. In ^1H NMR spectra of the Me-PDP, singlet at 3.9 ppm belongs to methoxy protons (—OCH_3) [29]. In ^{13}C NMR spectra, peak at 153.2 ppm belongs to two C_3 atoms and peak at 72.4 ppm corresponds to C_4 carbon atom (pyrazole ring). Carbonyl, C_2 has the highest chemical shifts and observed at 169.8 ppm. The peak of the acetate carbons (—$COCH_3$) appeared at 22.5 ppm for all of the phenylazo dyes. Aromatic carbon peaks are shown to be at approximately 100–140 ppm depends on the substituted positions. Methoxy carbon peak was observed at about 55.6 ppm for Me-PDP.

UV–Vis spectra of phenylazo dyes

The UV–Vis absorption spectra of the phenylazo dyes were recorded between 300 and 700 nm using a variety of solvents and concentrations (10^{-6}–10^{-8} M), and the results are shown in Fig. 4. The absorption maxima of the dyes were found to be independent of the solution phase and did not have a correlation with the dielectric constants of the solvents. Each of the phenylazo dyes gave a single dominant absorption peak. Additionally, as outlined in Table 2, there was no significant change observed with the use of chloroform, acetic acid, DMSO, DMF, acetonitrile and methanol. The absorption maxima of the phenylazo dyes in the corresponding solvents are similar. We observed that in DMSO and DMF,

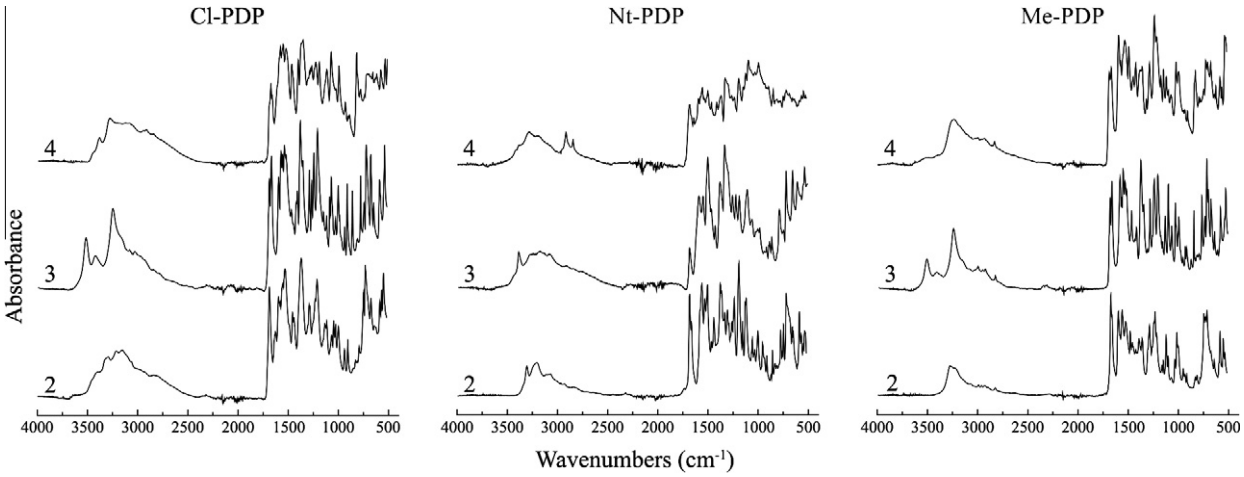


Fig. 1. The experimental FT-IR spectrums of phenylazo dyes.

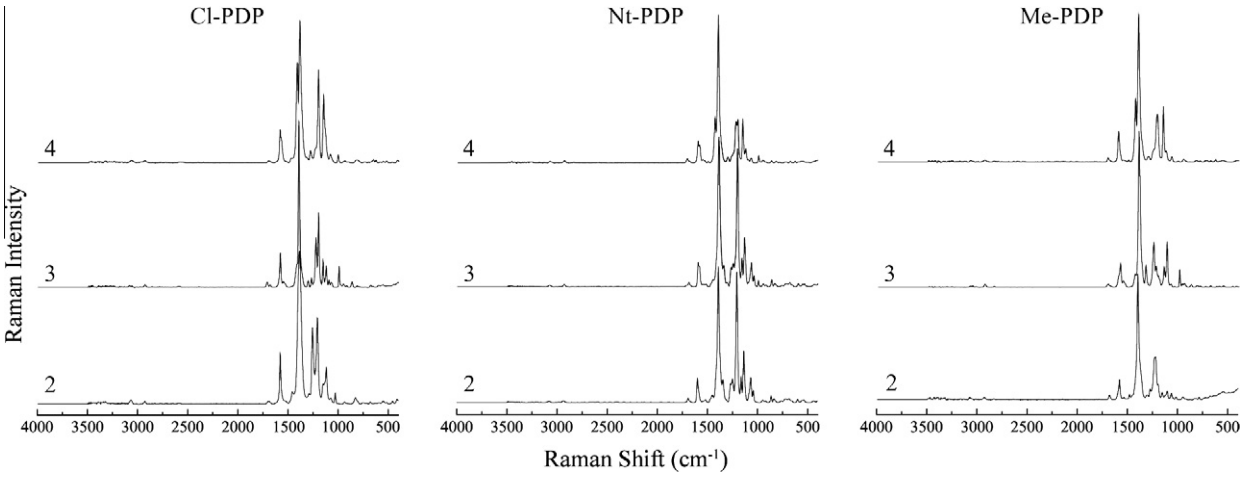


Fig. 2. The experimental Raman spectrums of phenylazo dyes.

the λ_{max} of the 4Nt-PDP dye bathochromically shifted with respect to the λ_{max} in other solvents (e.g., for 4Nt-PDP λ_{max} is 443 nm in DMSO, 427 nm in DMF and ~394 nm in other solvents).

The effects of the substituents on the dyes were also studied. The differences in the absorption spectra for the dye solutions can be assessed in terms of the dye structures. Details of the visible absorption spectra of the azopyrazole dyes that contain electron accepting substituents and electron donating substituents are shown in Table 2. When the substituents were in the *p*- and *o*-positions of the benzene rings, the λ_{max} of the dyes showed significant bathochromic shifts in all of the solvents. Greater bathochromic shifts were observed for *o*-substituted benzene rings than for *p*-substituted benzene rings, except for nitro groups. Whereas the *p*- and *o*-substituents showed electron withdrawing or donor properties owing to their inductive effects and resonance effects, the *m*-substituents showed only inductive effects. As a result of these greater electronic effects, the dispersion of electrons was more affected. The $-OCH_3$ and $-NO_2$ groups that possess greater resonance effects, showed significant bathochromic shifts in the *p*- and *o*-positions of the benzene rings. The results we obtained were in accord with these electronic effects.

The effects of acid, base and concentration on the absorption of the dye solutions were investigated, and the results are shown in Table 2. As seen in the table, the absorption spectra λ_{max} of the dyes in concentrated methanol are similar to the absorption spectra of the dyes in diluted methanol. When acetic acid (0.1 M) and piperidine (0.1 M) were added to the dye solutions in diluted methanol, the absorption spectra of λ_{max} of the dyes did not significantly shift.

Molecular geometry

The optimized structural parameters of the phenylazo dyes were calculated using the DFT-B3LYP level with the 6-31G(d) basis set. The optimized structures for the phenylazo dyes are shown in Fig. S1 (Supplementary information). 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazole is comprised of a two-rings (phenyl and pyrazole) system, and the rings are connected to each other by the azo group (N=N). The N=N bond length is 1.252 Å, and the average length of the N=N bonds in the phenylazo dyes vary from 1.2779 to 1.2791 Å. The lengthened N=N distance of the phenylazo dyes is the result of intramolecular hydrogen bonds [30] and conjugation in the two rings [16]. The length of the N=N bonds in the phenylazo dyes is longer than the N=N bonds in 4-(phenylazo)-3,5-diasetamido-1H-pyrazole [16] because of steric hindrance. The total energies of the azo and hydrazo forms of the phenylazo dyes are given in Table 3. The results indicate that the phenylazo dyes are in the azo form in the gas phase, and the stability of phenylazo dyes increases as the substitution number of the azo dye increases from 2 to 4.

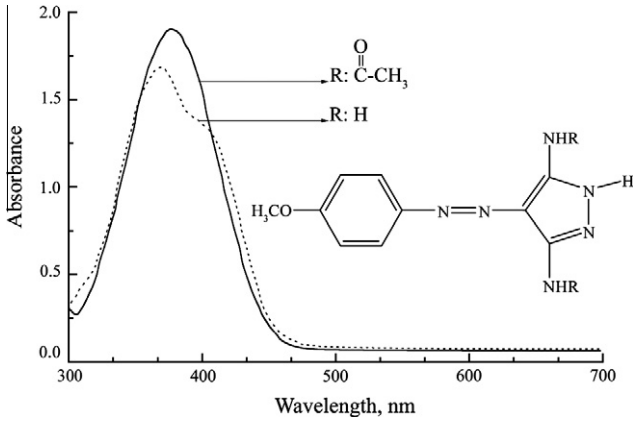


Fig. 3. Absorption spectra of 4-(methoxyphenylazo)-3,5-diamino-1H-pyrazoles and 4-(methoxyphenylazo)-3,5-diacetamido-1H-pyrazoles.

The phenylazo dyes can exist in four possible tautomeric forms, namely the azo-amine form (a), the hydrazo-amine form (b), the azo-imine form (c) and the hydrazo-imine form (d), as shown in Scheme 2. The hydrazo form of the compounds, which has hydrogen atoms present in the α- and β- positions, is more stable. Therefore, we expected that the phenylazo dyes are present in the hydrazo-amine (b) and hydrazo-imine (d) forms. The UV spectra of the 4-(substituted phenylazo)-3,5-diamino-1H-pyrazoles produced a shoulder; however, this shoulder disappeared when all of the phenylazo dyes were acetylated (Fig. 3). This result suggests that the phenylazo dyes are present as a single tautomeric form in all of the solvents used.

The dyes can exist in the hydrazo and azo tautomeric forms, but the spectroscopic and optimized structural parameter results suggest that these phenylazo dyes are predominantly in the azo (Scheme 2c) form in solution and in the solid state.

Antimicrobial activity of phenylazo dyes

The synthesized phenylazo dyes were tested for their antimicrobial activity against bacterial strains: *B. cereus* RSKK 863, *S. aureus* ATCC 259231, *M. luteus* NRLL B-4375, *E. coli* ATCC 11230 and

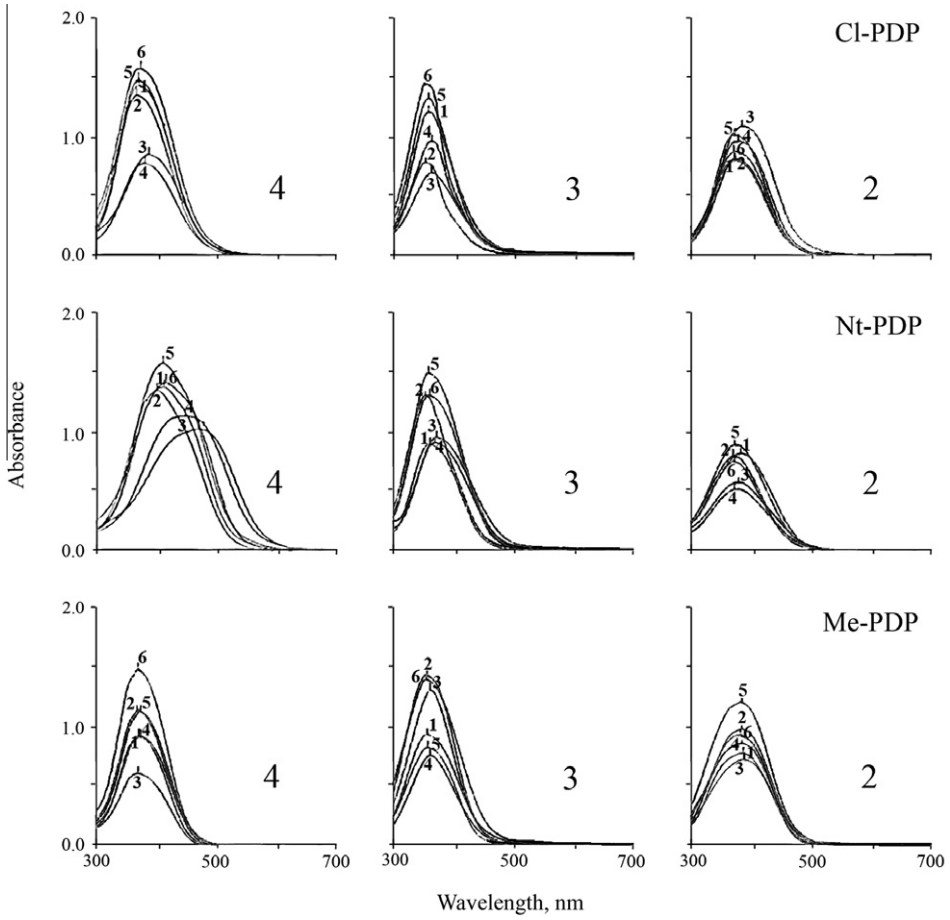


Fig. 4. Absorption spectra of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles in chloroform (1), acetic acid (2), DMSO (3), DMF (4), acetonitrile (5) and methanol (6).

Table 2
Influence of solvent on λ_{max} (nm) of azo dyes.

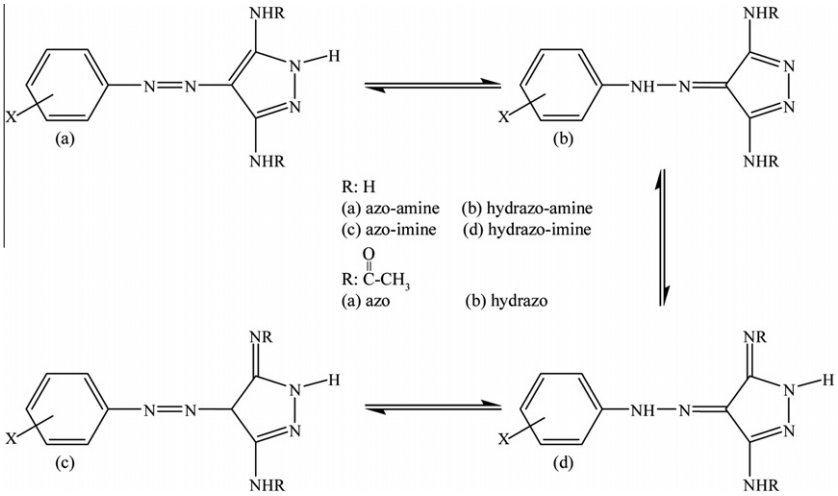
Dye	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform	Methanol (10^{-6} M)	Methanol (10^{-8} M)	Methanol (acid)	Methanol (base)
2Cl-PDP	382	378	371	369	370	371	369	369	367	369
3Cl-PDP	363	363	358	351	354	357	351	355	353	354
4Cl-PDP	371	370	361	362	356	361	362	363	359	357
2Nt-PDP	376	378	370	371	371	383	371	371	371	371
3Nt-PDP	371	369	360	361	354	360	361	359	355	359
4Nt-PDP	443	427	396	396	386	394	396	394	393	411
2Me-PDP	389	386	383	382	383	385	382	381	383	380
3Me-PDP	361	360	358	355	357	357	355	355	356	356
4Me-PDP	371	371	370	369	368	370	369	369	365	365

yeast; *C. albicans* ATCC 10239 by the disk diffusion method. The antimicrobial activity results are given in Table 4. The best results were obtained for compound 2Cl-PDP against the microorganisms, and a similar effect was noted for 4Cl-PDP. Generally, the 2Cl-PDP and 4Cl-PDP dyes were the most active, but 3Cl-PDP showed no inhibition in the growth of the microorganisms. The Nt-PDP dyes had higher antibacterial activity than Me-PDP dyes, but they had lower activity than Cl-PDP. Antibacterial effect of some antibiotics was investigated as detailed elsewhere [31–35]. Compared to antibiotics, phenylazo dyes showed lower activity except for 2Cl-PDP and 4Cl-PDP against *E.coli*, *S. aureus*, *M. luteus* and *B. cereus*. Antibacterial activity of 2Cl-PDP and 4Cl-PDP dyes is very close to some antibiotics such as ampicillin [32], tetracycline [31] and erythromycin [35] against *E. coli* and *B. cereus*.

The Cl atoms play a vital role in various metabolic systems in these microorganisms. Moreover, the position of Cl atoms is particularly important. The Me-PDP and Nt-PDP dyes show varying degrees of inhibition of the growth of the microorganisms. These

Table 3
Calculated total energies (E) of the azo and hydrazo form of azo dyes.

Dye	Tautomer	
	Azo	Hydrazo
2Cl-PDP	−1442.35195822	−1442.31132906
3Cl-PDP	−1442.35209481	−1442.32615779
4Cl-PDP	−1442.35224307	−1442.32661301
2Nt-PDP	−1187.24791636	−1187.20887164
3Nt-PDP	−1187.25653618	−1187.21438208
4Nt-PDP	−1187.25767314	−1187.23180144
2Me-PDP	−1097.27051341	−1097.22872347
3Me-PDP	−1097.27770344	−1097.24264651
4Me-PDP	−1097.28002072	−1097.25352025



Scheme 2. Molecular structure and tautomers of phenylazo dyes with different R substituents.

Table 4
Antimicrobial activities of azo dyes.

Dye	Inhibition zone diameter (mm)				
	E coli ATCC 11230	*S aureus* ATCC 259231	*M luteus* NRRL B-4375	*B cereus* RSKK 863	*C albicans* ATCC 10239
2Cl-PDP	24/26/28	6/6/6	10/10/10	20/20/20	12/12/8
3Cl-PDP	–	–	–	–	–
4Cl-PDP	16/16/16	14/14/14	18/20/20	16/16/16	20/22/18
2Nt-PDP	8/8/8	6/6/6	4/6/6	6/4/4	20/18/18
3Nt-PDP	4/4/4	8/8/8	10/10/8	10/10/12	4/2/4
4Nt-PDP	–	–	–	8/10/10	16/18/18
2Me-PDP	10/12/12	8/10/10	–	10/10/10	–
3Me-PDP	8/10/12	–	–	–	16/12/16
4Me-PDP	18/22/20	–	–	10/8/10	6/6/6

dyes (Table 4) have a more profound effect upon the growth of *E. coli, B. cereus* and *C. albicans*. Unfortunately, there was no relationship between the position of the substituents and antimicrobial activity for the phenylazo dyes.

Conclusions

In this article, 4-(substituted phenylazo)-3,5-diamino-1H-pyrazoles were synthesized from 2-(substituted phenylazo) malononitriles.

The calculated geometric parameters and vibrational frequencies are in good agreement for some of the bands. However, the differences between the observed and calculated wavenumber values for the N—H and C=O groups are large because of the presence of the intermolecular interactions in the solid state. The ATR-FTIR, ^{1}H NMR, UV and theoretical studies showed that, for the phenylazo dyes, the azo form predominated. Moreover, for the first time to our knowledge, the synthesized phenylazo dyes were tested for their biological activity, and the phenylazo dyes showed varying degrees of inhibition on the growth of the microorganisms. As a consequence, we can conclude that the newly synthesized 2Cl-PDP and 4Cl-PDP phenylazo dyes could be leads for the development of antimicrobial materials. Ongoing studies are focused on the development of antimicrobial materials using 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazole molecules.

Acknowledgement

The authors thank Prof. T. Uyar for his encouragement and useful discussions.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.12.074.

References

[1] T.S. Natarajan, K. Natarajan, H.C. Bajaj, R.J. Tayade, Ind. Eng. Chem. Res. 50 (2011) 7753–7762.
[2] L. Peng, J. Zhai, D. Wang, Y. Zhang, Q. Zhao, P. Wang, S. Pang, Z. Fan, T. Xie, Photochem. Photobiol. Sci. 8 (2009) 875–880.
[3] M.A. Kamboh, I.B. Solagi, S.T.H. Sherazi, S. Memon, J. Hazard. Mater. 172 (2009) 234–239.
[4] M. Snehalatha, C. Ravikumar, I.H. Joe, Solid State Sci. 11 (2009) 1275–1282.
[5] R. Rajendran, S.K. Sundaram, K.U. Maheswari, J. Environ. Sci. Technol. 4 (2011) 568–578.
[6] P.P. Kasture, Y.A. Sonawane, R.N. Rajule, G.S. Shankarling, Color. Technol. 126 (2010) 348–352.
[7] T. Aysha, S. Lunak Jr., A. Lycka, R. Hrdina, Dyes Pigments 91 (2011) 170–176.
[8] M.M.M. Raposo, A.M.F.P. Ferreira, M. Amaro, M. Belsley, J.C.V.P. Moura, Dyes Pigments 83 (2009) 59–65.
[9] P.C. Tsai, I.J. Wang, Dyes Pigments 76 (2008) 575–581.
[10] J.H. Choi, J.S. Park, M.H. Kim, H.Y. Lee, A.D. Tows, Color. Technol. 123 (2007) 379–386.
[11] A.C. Lucilha, C.E. Bonancea, W.J. Barreto, K. Takashima, Spectrochim. Acta A 75 (2010) 389–393.
[12] G. Pavlovic, L. Racane, H. Cicak, V.T. Kulenovic, Dyes Pigments 83 (2009) 354–362.
[13] A.M. Asiri, I.M.I. Ismail, K. Al-Amry, N.A. Fatani, Dyes Pigments 67 (2005) 111–115.
[14] J. Suesat, T. Mungmeechai, P. Suwanruji, W. Parasuk, J.A. Taylor, D.A.S. Phillips, Color. Technol. 127 (2011) 217–222.
[15] N. Biswas, S. Umapathy, J. Phys. Chem. A 104 (2000) 2734–2745.
[16] S. Kinali, S. Demirci, Z. Calisir, M. Kurt, A. Atac, J. Mol. Struct. 993 (2011) 254–258.
[17] A.C. Razus, L. Birzan, M. Cristea, E.M. Ungureanu, M.S. Cretu, Dyes Pigments 86 (2010) 1–5.

[18] M. Boiko, T. Vrublevska, O. Korkuna, G. Teslyar, Spectrochim. Acta A 79 (2011) 325–331.
[19] Z. Seferoglu, E. Aktan, N. Ertan, Color. Technol. 125 (2009) 342–351.
[20] R. Dong, Y. Liu, Y. Zhou, D. Yan, X. Zhu, Polym. Chem. 2 (2011) 2771–2774.
[21] S. Tamesue, Y. Takashima, H. Yamaguchi, S. Shinkai, A. Harada, Angew. Chem. Int. Ed. 49 (2010) 7461–7464.
[22] H. Jin, Y. Zheng, Y. Liu, H. Cheng, Y. Zhou, D. Yan, Angew. Chem. Int. Ed. 50 (2011) 10352–10356.
[23] G.D. Fu, L.Q. Xu, F. Yao, G.L. Li, E.T. Kang, ACS Appl. Mater. Interfaces 1 (2009) 2424–2427.
[24] M.H. Elnagdi, E.M. Kandeel, E.M. Zayed, Z.E. Kandil, J. Heterocycl. Chem. 14 (1977) 155–157.
[25] M.J. Frisch et al., Gaussian, Inc., Wallingford CT, 2009.
[26] A. Frish, A.B. Nielsen, A.J. Holder, Gauss View User Manual, Gaussian Inc., Pittsburg, PA, 2001.
[27] J.B. Foresman, A.E. Frisch, Exploring Chemistry with Electronic Structure Methods, Second ed., Gaussian Inc., Pittsburgh, PA, 1996.
[28] J. Dostanic, V. Natasa, G. Uscumlic, D. Mijin, J. Serb. Chem. Soc. 76 (2011) 499–504.
[29] Y. Li, B.O. Patrick, D. Dolphin, J. Org. Chem. 74 (2009) 5237–5243.
[30] M. Snehalatha, C. Ravikumar, N. Sekar, V.S. Jayakumar, I.H. Joe, J. Raman. Spectrosc. 39 (2008) 928–936.
[31] S. Çete, A. Dişli, Y. Yıldırır, A. Yaşar, Asian J. Chem. 18 (2006) 2061–2066.
[32] N. Özbek, G. Kavak, Y. Özcan, S. İde, N. Karacan, J. Mol. Struct. 919 (2009) 154–159.
[33] P.L. Ho, K.H. Chow, K.Y. Yuen, W.S. Ng, P.Y. Chau, J. Antimicrob. Chemother. 42 (1998) 49–54.
[34] S. Alyar, H. Zengin, N. Özbek, N. Karacan, J. Mol. Struct. 992 (2011) 27–32.
[35] C. Gaudreau, H. Gilbert, J. Antimicrob. Chemother. 39 (1997) 707–712.