Research Article

Synthesis of Novel Heterocyclic Imine Type UV Absorbers for Application on Cotton Based Textile Materials

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Novel Schiff bases with the potential to exhibit biologically active and UV absorption properties were synthesized. Their application on cotton based textile materials was performed and the UV protection factor (UPF) values and the antibacterial features of the treated fabrics were measured.

1. Introduction

Heterocyclic compounds are found in many natural and synthetic products with a wide range of pharmacological activities, such as antiviral, anticancer, antibacterial, antifungal, anticonvulsant, antiparkinsonian, and anti-inflammatory, that can be well illustrated by the large number of drugs in the market containing these functional groups. In recent years, many heterocyclic compounds have been synthesized and their biological activities researched. In particular the behavior of heterocyclic compounds against cancer cells has been investigated [1, 2]. At the beginning of the 20th century, five-membered heterocyclic compounds such pyrrole, imidazole, thiazole, oxazole, pyrazole, indole, and thiazolidinones have attracted great interest among pharmaceutical chemists, because of their usage as raw materials for drugs [3–5]. As a result of over 100 years of investigation on heterocyclic compounds, it is clear that the usage of nitrogen, oxygen, and sulfur containing structures in bioactive compounds allows for tremendous variability. On the other hand, these types of compounds are gaining in importance owing to their UV absorption characteristics [6–8]. Sunlight includes significant UV radiation, which can be destructive to human health. It is known that long term exposure to UV radiation causes harmful effects on the human skin, some of which are sunburn, erythema, skin ageing, and, most importantly, the risk

of skin cancer. In this case, the use of protective textile garments becomes a focus of great interest. UV radiation also causes unfavorable effects on synthetic materials. For greater protection from this exposure, the use of UV absorbing materials in textiles is needed.

Imines, also known as azomethines or Schiff bases, are condensation products of primary amines with carbonyl compounds. Imines also have a wide range of biological activities, including antifungal, antibacterial, anti-inflammatory, and antiviral activities [9–11]. Schiff bases are used in industrial applications such as photostabilization of poly(vinyl chloride) [12, 13], poly(methyl methacrylate) [12], and polystyrene from photodegradation by their addition to polymer films [14].

The most common method for Schiff base synthesis is the reaction of an aldehyde or a ketone with a primary amine with elimination of a water molecule. This reaction is mostly accomplished by acid catalysis to obtain the products in good yields. For removal of water, several dehydrating agents have been used such as sodium sulfate. In addition, alternative methods, including tetramethyl orthosilicate or trimethyl orthoformate, have been reported [15–17]. As catalysts, mineral acids, organic acids, and Lewis acids have been reported [18–21]. Several synthesis techniques for Schiff bases have been reported, including solvent-free methods, microwave,

FIGURE 1: Synthesis of compounds 1–4.

and ultrasound methods as well as the use of water suspension medium, liquid crystals, and molecular sieves [22–32].

We recently prepared several new bis(indolyl)methanes and their UV absorbing behaviors were investigated both in solution and in polymer substrates [33]. After successful results, several new Schiff bases (aldimines) were prepared by condensation of 5-amino-3-methylisoxazole which was chosen similarity of active group of epiboxidine which are reported as potent nicotinic receptor [34] with aryl aldehydes as described in Section 3 and their UV absorbing behaviors were investigated. Imine compounds which were prepared easily in good yields have been selected due to conjugation to improve UPF values of cotton fabric.

2. Results and Discussion

2.1. Synthesis. Condensation of 5-amino-3-methylisoxazole with 1-naphthaldehyde, 2-naphthaldehyde, 1-pyrenecarbaldehyde, and phenanthrene-9-carbaldehyde in the presence of *p*-toluenesulfonic acid (TsOH; except 4) gave aldimine compounds 1–4 (Figure 1).

The structures of new aldimines were firmly established on the basis of IR, NMR, and mass spectra which were in agreement with the proposed structures. Introduction of aryl aldehydes onto isoxazole ring chromophore improved their UV absorbances (Table 1). From their UV spectra it is easy to

TABLE 1: Properties of new compounds.

Product	Time (min)	Yield (%)	Mp (°C)	$\lambda_{\max}/\text{nm}$ (absorbance)
1	240	54	90–92	350 (0.87)
2	240	58	195–197	385 (0.80)
3	2	36	159–162	425 (1.10)
4	1200	42	170–171	360 (1.20)

see why compounds 1–4 are excellent UV absorber chromophores. Figure 2 shows the UV spectra of compounds 1 and 4, respectively. The ^1H NMR spectra of 1–4 displayed singlets at 9.80–9.42 ppm due to the imine protons in addition to other signals. In the IR spectra of the compounds, carbonyl bands were absent which clearly confirmed that a condensation with the aryl aldehydes had taken place.

2.2. Textile Applications. For textile applications, compounds 1–4 were dissolved in dichloromethane, mixed with printing paste, and applied on 100% cotton undyed fabrics. The raw and all printed fabrics were subjected to AATCC 183:2014 (The American Association of Textile Chemists and Colorists. Transmittance or Blocking of Erythemally Weighted Ultraviolet Radiation through Fabrics; AATCC: Research Triangle

FIGURE 2: UV spectra of compounds **1** and **4**, respectively.

TABLE 2: UV protective features of absorbers.

UV absorber printed fabric	UVA transmittance* (315–400 nm)	UVB transmittance* (280–315 nm)	UPF	UVA blocking (%)	UVB blocking (%)	UPF label
Reference	5.65	2.02	33.37	94.35	97.98	27
1	0.27	0.05	1709.2	99.73	99.50	40+
2	2.72	0.15	223.52	97.28	99.85	40+
3	0.27	0.13	531.89	99.73	99.87	50+
4	2.93	0.05	307.60	97.07	99.95	50+

* Average.

Park, NC, USA, 2014) standard tests at 21°C temperature and 66% relative humidity.

These results show that the UPF: 27 value of standard fabric increases up to 40+ and 50+ upon Schiff base treatments. According to standard specimens, a UPF value of 15–24 is good, 25–39 is very good, and 40 or greater is excellent UV-protection category. That means both UVA and UVB transmission through fabrics decreased and excellent protection obtained (Table 2). All printed fabrics were washed 25 times according to BS EN ISO 6330 5A standard (Domestic washing and drying procedures for textile testing. Available online: <https://www.iso.org/obp/ui/#iso:std:43044:en> (accessed on 15 March 2012)), 6330 5A standard [26]. The UPF values were also tested after 25 washing cycles. The UPF values are the same as the unwashed fabrics, at 40+. In accordance with this, we still have the protective property after multiple washing cycles. After connecting to the fabric of the imine compounds have been shown to be binding strongly.

Antibacterial activities were tested according to AATCC147-2011 standard (available online: <https://www.oeko-tex.com/en/manufacturers/manufacturers.xhtml>, (accessed on 5 February 2016)), at 37 ± 2°C temperature and 18–24 h incubation time for *Staphylococcus aureus* (AATCC 6538 Gram+) microorganism (Antibacterial Activity Assessment

TABLE 3: Antibacterial features of absorbers.

Fabric printed	Washes	Bacteria growth	Inhibition zone (mm)*
reference	–	+	
1	25	–	0
2	25	–	0
3	25	–	0
4	25	–	0

* Width of clear zone of inhibition (positive = there is bacterial growth; negative = there is not bacterial growth).

of Textile Materials). The results show the antibacterial activities achieved (Table 3). Furthermore, we tested the coated fabrics and compared them to the OEKO TEX 100 standard for PAH (polyaromatic hydrocarbon), APEO (alkylphenyl ethylate), and phthalate contents. According to the results, it can be said that the fabrics do not have toxic properties.

3. Experimental

3.1. General Information. Reactions were monitored using thin-layer chromatography (TLC). The crude products were

purified by silica gel chromatography with a solvent mixture to afford the title compounds. UV absorption spectra were recorded on an Agilent Technologies 8453 spectrophotometer. IR spectra were obtained with a "Perkin Elmer, FT-IR" system and are reported in terms of frequency of absorption (cm^{-1}). Melting points were determined with a "Gallenkamp" digital thermometer. All melting points are uncorrected. NMR spectra were determined with a "Bruker Ac-500 MHz NMR." TMS (tetramethylsilane) was used as internal standard and CDCl_3 was used as the solvent. Signal multiplicities in the NMR spectra are reported as follows: s-singlet, brs-broad singlet, d-doublet, dd-doublet of doublets, and m-multiplet. Mass spectra were measured with Agilent 6890N GC-System-5973 MSD or Agilent LC-MSD Trap SL. All tests related to textile applications are done by 3rd party laboratories having accreditation. Tests for transmittance or blocking of erythemally weighted ultraviolet radiation through fabrics (AATCC 183:2014) tests were performed at Intertek laboratories, Istanbul, Turkey. Domestic washing and drying procedures for textile (BS EN ISO 6330 5A) tests were made in Sanko holding-ISKÖ division R&D laboratories Bursa/Turkey. Antibacterial activity assessment of textile materials (AATCC147-2011) tests were performed at Ekoteks laboratories, Istanbul, Turkey.

3.2. Synthesis of 1–4

N-(3-Methylisoxazol-5-yl)-1-(naphthalen-1-yl)methanimine (**1**). 5-Amino-3-methylisoxazole (3 mmol) and 1-naphthaldehyde (3 mmol) were dissolved in 12 mL of anhydrous toluene under nitrogen atmosphere. *p*-Toluenesulfonic acid (TsOH) (0.3 mmol) and molecular sieve (3 g, previously activated at 140°C for 4 days) were added and refluxed for 4 h. The progress of the reaction was monitored by TLC. The residue was filtered, toluene was evaporated, and crude compound **1** was recrystallized from acetonitrile in an ultrasonic bath. Yellow crystals; mp: $90\text{--}92^\circ\text{C}$, Yield = 58%; R_f = 0.28 (1:5; EtOAc/*n*-hexane); FTIR (ATR): ν = 3050, 2918, 2849, 1618, 1595, 1562, 1442, 1414, 1337, 1175, 732, 693 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ = 1.88 (s, 3H, CH_3), 6.38 (s, 1H, =CH), 7.34–7.51 (m, 4H, ArH), 7.81 (d, J = 8.51 Hz, 1H, ArH), 7.92 (dd, J = 8.19; 11.65 Hz, 1H, ArH), 8.66 (d, J = 8.51 Hz, 1H, ArH), 9.45 (s, 1H, =CH) ppm; ^{13}C NMR (CDCl_3 , 125 MHz): δ = 12.35 (CH_3), 111.19 (CH), 123.57 (CH), 125.28 (CH), 126.34 (CH), 127.89 (CH), 128.82 (CH), 130.51 (CH), 130.87 (CH), 131.70 (Cq), 133.42 (Cq), 133.62 (Cq), 161.21 (Cq), 162.23 (Cq) ppm; UV (λ_{max} , CH_2Cl_2): 385 nm (c = 1.5×10^{-4} , A = 0.80, ϵ = 5.4×10^3); LC-MS (ESI): m/z = 236 (M^+) for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$.

N-(3-Methylisoxazol-5-yl)-1-(naphthalen-2-yl)methanimine (**2**). 5-Amino-3-methylisoxazole (5 mmol) and 2-naphthaldehyde (5 mmol) were dissolved in 20 mL anhydrous toluene under nitrogen atmosphere. *p*-Toluenesulfonic acid (TsOH) (0.3 mmol) and molecular sieve (3 g, previously activated at 140°C for 4 days) were added and refluxed for 4 h. The progress of the reaction was monitored by TLC. The residue was filtered, toluene was evaporated, and crude product **2** was recrystallized from methanol in an ultrasonic bath. Yellow

crystals; mp: $195\text{--}197^\circ\text{C}$, Yield = 54%; R_f = 0.31 (1:5; EtOAc/*n*-hexane); FTIR (ATR): ν = 3055, 2927, 2890, 1595, 1576, 1438, 1411, 1373, 1176, 753, 693 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ = 2.34 (s, 3H, CH_3), 6.01 (s, 1H, =CH), 7.54–7.61 (m, 2H, ArH), 7.88–7.96 (m, 3H, ArH), 8.14 (d, J = 9.77 Hz, 1H, ArH), 8.26 (s, 1H, ArH), 8.99 (s, 1H, =CH) ppm; ^{13}C NMR (CDCl_3 , 125 MHz): δ = 12.33 (CH_3), 96.66 (CH), 123.68 (CH), 126.97 (CH), 127.93 (CH), 128.44 (CH), 128.87 (CH), 129.03 (CH), 132.97 (Cq), 133.36 (Cq), 135.70 (Cq), 138.17 (Cq), 161.66 (Cq), 163.42 (CH) ppm; UV (λ_{max} , CH_2Cl_2): 350 nm (c = 1.7×10^{-7} , A = 0.875, ϵ = 5.16×10^6); GC-MS (EI, 70 eV): m/z = 236 (M^+) for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$.

N-(3-Methylisoxazol-5-yl)-1-(phenanthren-9-yl)methanimine (**3**). 5-Amino-3-methylisoxazole (1 mmol), *p*-toluenesulfonic acid (TsOH) (5 mg), and 1-pyrenecarbaldehyde (1 mmol) were dissolved in minimum amount of absolute ethanol in an ultrasonic bath. Silica gel (40 mg) was added to the mixture and the reaction was sonicated at 360 W. The reaction was completed in 2 min. The progress of the reaction was monitored by TLC. The residue was filtered and the crude product **3** was purified by column chromatography (1:5; EtOAc/*n*-hexane). Yellow crystals; mp: $159\text{--}162^\circ\text{C}$, Yield = 36%; R_f = 0.30 (1:5; EtOAc/*n*-hexane); FTIR (ATR): ν = 3040, 2921, 2851, 1584, 1568, 1505, 1441, 1408, 1322, 1186, 717, 694 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ = 2.31 (s, 3H, CH_3), 6.11 (s, 1H, =CH), 8.01 (dd, J = 7.56; 9.77 Hz, 2H, ArH), 8.13 (dd, J = 8.19; 12.29 Hz, 2H, ArH), 8.19–8.22 (m, 3H, ArH), 8.70 (d, J = 8.19 Hz, 1H, ArH), 8.88 (d, J = 9.77 Hz, 1H, ArH), 9.80 (s, 1H, =CH) ppm; ^{13}C NMR (CDCl_3 , 125 MHz): δ = 12.12 (CH_3), 96.84 (Cq), 97.28 (CAr), 98.32 (Cq), 122.01 (CAr), 124.44 (Cq), 124.89 (Cq), 126.40 (CAr), 126.61 (CAr), 126.82 (CAr), 126.96 (CAr), 127.37 (CAr), 129.77 (CAr), 129.87 (CAr), 130.05 (CAr), 130.48 (Cq), 131.18 (Cq), 131.79 (Cq), 134.71 (Cq), 161.40 (CH), 161.89 (Cq) ppm; (λ_{max} , CH_2Cl_2): 425 nm (c = 7.78×10^{-6} , A = 1.1, ϵ = 1.8×10^4); LC-MS (ESI): m/z = 236 (M^+) for $\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}$.

N-(3-Methylisoxazol-5-yl)-1-(pyren-1-yl)methanimine (**4**). 5-Amino-3-methylisoxazole (1 mmol) was dissolved in 2 mL of absolute methanol at room temperature. Phenanthrene-9-carbaldehyde (1 mmol) and molecular sieve were added and the mixture was refluxed for 20 h. The progress of the reaction was monitored by TLC. Compound **4** was purified by column chromatography (1:5; EtOAc/*n*-hexane). Yellow crystals; mp: $170\text{--}171^\circ\text{C}$, Yield = 52%; R_f = 0.28 (1:5; EtOAc/*n*-hexane); FTIR (ATR): ν = 3051, 2917, 1600, 1564, 1526, 1489, 1438, 1409, 1369, 1194, 745, 711 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ = 2.30 (s, 3H, CH_3), 6.09 (s, 1H, =CH), 7.57–7.60 (m, 1H, ArH), 7.67–7.72 (m, 3H, ArH), 7.95 (d, J = 7.88 Hz, 1H, ArH), 8.37 (s, 1H, ArH), 8.63 (d, J = 8.19 Hz, 1H, ArH), 8.69–8.71 (m, 1H, ArH), 9.09–9.11 (m, 1H, ArH), 9.42 (s, 1H, =CH) ppm; ^{13}C NMR (CDCl_3 , 125 MHz): δ = 12.20 (CH_3), 97.36 (CAr), 122.80 (CAr), 123.19 (CAr), 125.17 (CAr), 127.26 (CAr), 127.29 (CAr), 127.70 (CAr), 129.33 (CAr), 130.25 (Cq), 130.64 (Cq), 134.79 (CAr), 163.55 (CH) ppm; (λ_{max} , CH_2Cl_2): 360 nm (c = 1.48×10^{-5} , A = 1.20, ϵ = 8.1×10^4); GC-MS (EI, 70 eV): m/z = 286 (M^+) for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}$.

4. Conclusions

In conclusion, we have prepared a new series of aryl aldimines which can be used as UV absorbers in the textile industry. They increased the UV protection factor of undyed fabric up to 40+ and 50+ from 27. This shows that they are quite active as UV absorbers. Furthermore, all printed fabrics were washed 25 times according to standard procedure with minimal loss of UV protection. Tests results also indicated that the imine compounds exhibit antibacterial properties.

Competing Interests

The authors declare that they have no competing interests.

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