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Synthesis of a Novel Cationic Dye to Impart Mosquito-Repellent and UV Protection to an Acrylic Fabric

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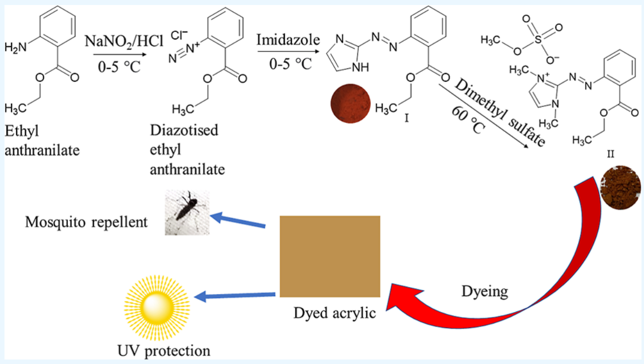
ABSTRACT: The growing demand for innovative routes to develop functional textiles initiated the necessity of new efficient functional molecules. Dyes can provide durable functional protection to textiles due to their ability to generate strong dye−fiber interaction. New dyes to improve a dyed substrate's quality and aesthetic appearance are in huge demand. This research aims to prepare a mosquito-repellent and UV-protective acrylic fabric using a novel cationic (basic) dye. The cationic dye was synthesized and thoroughly characterized with the help of FTIR, ^{1}H NMR, ^{13}C NMR, and CHN analysis. The dye was further used for the dyeing of the acrylic fabric by using an infrared dyeing machine. To analyze the suitability of dyed fabrics for daily use, washing, rubbing, and light fastness of dyed fabrics were determined. The amount of dye (%) taken up by the acrylic fabric (exhaustion %) was determined, and more than 72% of exhaustion was obtained. The fixation (%) of the dye on acrylic fabrics was also quantified, and more than 80% fixation was obtained. The coloration properties of the dyed fabrics (L^*, a^*, b^*, and K/S) were examined. The dyed fabrics showed a K/S of more than 3. The mosquito-repellent action provided by the dyed fabrics was also analyzed, and 100% repellency was obtained. The dyed fabrics provided an excellent UV-protective property. The multifunctional properties of dyed fabrics were retained significantly even after laundering treatments. The dyed fabrics were characterized using X-ray diffraction and thermogravimetric analysis. A reduction in crystalline peak intensity after dyeing was obtained. The dyed and undyed fabrics were also tested for their tensile strength.



1. INTRODUCTION

Dyes make human life fascinating, and the demand for dye molecules possessing functional properties such as mosquito repellency and UV protection is gradually going up. Basic dyes are cationic in nature and utilized to dye various textile substrates, including acrylic and nylon. Ma et al. synthesized antimicrobial cationic dyes by reacting anthraquinone derivatives with *N*,*N*-dimethylbutylamine.[1] Alkyl quaternary ammonium salt-based antimicrobial azo dye was prepared by Liu et al.[2] A quaternary group-based cationic disperse reactive dye was prepared by Xie and Hou; the dye was applied to wool under acidic conditions to form a covalent linkage with the wool.[3] Deligeorgiev et al. prepared 2-(4-chlorophenylazo) imidazole-based cationic dyes.[4] Deligeorgiev and Simov prepared a cationic dye from *N*,*N*-disubstituted anilines and 2-amino-6-(2-chloroethoxy)benzothiazol.[5] A fluorescent dye having cationic nature was prepared using coumarin as a reactant, and acrylic fibers' coloration was targeted using this dye.[6] Cationic dyes were used to dye meta-aramid fiber under ultrasonic microwave irradiation.[7] A cationic dye based on azo naphthalimide was prepared by Shaki.[8]

Recently, various researchers have shown interest to prepare functional textiles.[9−15] Mosquito-repellent textiles are of particular interest to most consumers as it saves us from mosquito bites; thus, it protects us from various deadly diseases (malaria, dengue, chikungunya, and yellow fever). Citronella essential oil-based microcapsules were prepared by complex coacervation, and cotton fabrics finished with the microcapsules showed mosquito-repellent properties.[16] Tseghai used castor oil to generate mosquito-repellent cotton.[17] The microcapsules based on core materials (thyme oil, cypress oil, and grapefruit oil) were utilized as finishing agents to develop mosquito-repellent and UV-protective bamboo/TENCEL blended fabric.[18] Yu et al. prepared antimosquito polyester using bendiocarb/alphacypermethrin.[19] The mosquito-repellent efficiency of textiles finished with permethrin was explored by Ho et al.[20] Mosquito-repellent cotton was made using *Justicia adhatoda Vasica* extract.[21] Rana et al. used

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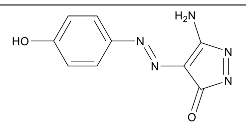
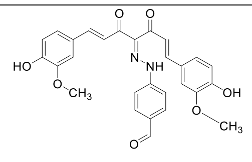
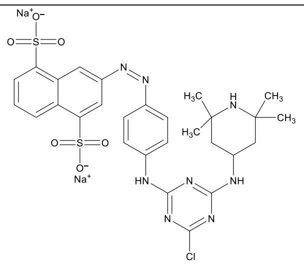
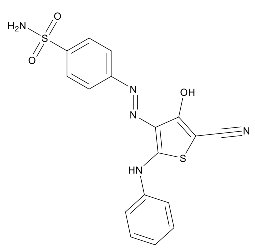
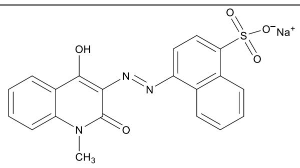
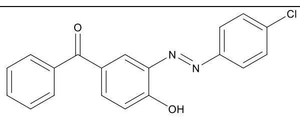
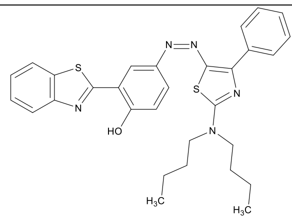
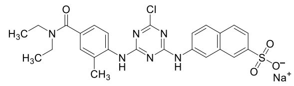
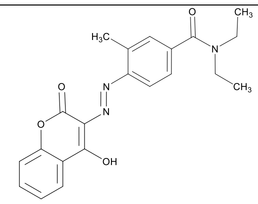
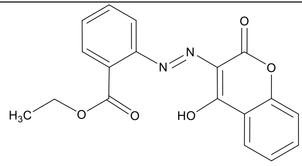
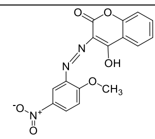
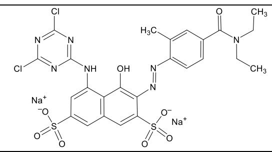
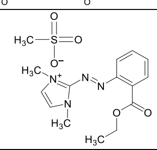
Table 1. Review of Literature Dealing with Functional Dyes

Structure of dye	Type of dye	Functional properties	Reference number
	Disperse dye	Antibacterial	40
	Disperse dye	Antibacterial	41
	Reactive dye	Antibacterial	42
	Disperse dye	Antibacterial	43
	Acid dye	UV protection	44
	Disperse dye	UV protection	45
	Disperse dye	Antibacterial and UV protection	46
	Reactive dye	Mosquito repellent	38
	Disperse dye	Mosquito repellent, antibacterial, and UV protection	9
	Disperse dye	Mosquito-repellent, antibacterial, and UV protection	9
	Disperse dye	Mosquito-repellent, antibacterial, and UV protection	47
	Reactive dye	Mosquito-repellent and UV protection	48
	Basic dye	Mosquito repellent and UV protection	Present work

marigolds to prepare mosquito-repellent cotton.[22] Kantheti et al. used *Ocimum basilicum* leaf extract to prepare mosquito-repellent printed textiles.[23] Anitha et al. prepared microcapsules based on lemongrass oil, and the polyester was finished with the prepared microcapsules to impart mosquito-repellent protection.[24] Ap dos Santos et al. prepared mosquito-repellent textiles using ethyl butylacetylamino-propionate as a mosquito repellent.[25] The authors prepared mosquito-repellent cotton using *Schinus molle* seed oil.[26] *Thymus vulgaris* oil-based microcapsules were utilized to develop the mosquito-repellent linen fabric.[27] Microcapsules containing cinnamon oil as a core and chitosan-gelatin as a shell was explored to develop multifunctional mosquito-repellent linen fabrics.[28] *Akarkara* was used to provide mosquito-repellent protection to cotton fabrics.[29] A combination of various oils (cinnamon, peppermint, and lavender) was explored to develop mosquito-repellent linen fabrics.[30] Orange peel extract was used to synthesize silver and zinc oxide nanoparticles; the finished fabric with the particles and extracts showed UV protection, antimicrobial, and mosquito-repellent activities.[31] The microcapsules loaded with rosemary oil were used to develop mosquito-repellent linen.[32]

Dyes that provide functional properties along with wash-durable color effects are urgently needed in textile industries. Azo dyes are the most widely used dyes[33,34] in the textile field due to their ease of synthesis and wide range of color availability. 1,4-Diaminoanthraquinone-based UV-protective acid dyes were developed.[35] A reactive dye based on 1-amino-8-naphthol-3,6-disulfonic acid was developed to impart UV protection to the cotton fabric.[36] Mokhtari et al. reported reactive dyes based on *N*,*N*-diethyl-*m*-toluamide (DEET) for imparting mosquito-repellent and antibacterial protection to nylon 6.[37] Singh and Sheikh prepared mosquito-repellent, antibacterial, and UV-protective cotton using the azoic dyeing

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method by the reaction of *Terminalia chebula* (a natural dye) and diazotized ethyl anthranilate.[11] Mosquito-repellent protection was imparted to nylon by using a reactive dye.[38] Azoic dyes for imparting mosquito-repellent protection to cotton were developed by reacting a derivative of DEET with different coupling components.[39] Disperse dyes containing a 4-hydroxycoumarin moiety were explored for multifunctional mosquito-repellent protection to polyester.[9] Table 1 summarizes the reports on structure, dye class, and functional properties.[40−48] The present work investigates the cationic (basic) dye for imparting mosquito repellency and UV protection properties to the acrylic fabric.

Due to the harmful impact of various mosquito repellents on humankind, nontoxic mosquito repellents are urgently required. Ethyl anthranilate has not shown any genetic toxicity.[49] Ethyl anthranilate has been considered an alternative to the most widely accepted mosquito repellent DEET.[50] A study suggested that a patch loaded with mosquito-repellent ethyl anthranilate has not generated any acute and dermal toxicity.[51] A study evaluated the toxicity of ethyl anthranilate against *Aedes albopictus* Skuse.[52] A study reported mosquito-repellent properties of ethyl anthranilate against *Aedes aegypti*.[53] Afify et al. reported a comparison of mosquito-repellent properties of ethyl anthranilate against methyl *N*,*N*-dimethyl anthranilate and butyl anthranilate.[54]

To the best of our knowledge, synthesis and application of mosquito-repellent basic dyes have not been found in the literature. Moreover, limited works have investigated the synthesis and application of mosquito-repellent dyes. In the present work, a novel basic dye was developed. Ethyl anthranilate was diazotized and reacted with imidazole; the product was further quaternized to make a basic dye. The synthesized basic dye was applied to the acrylic fabric at different shades (%). The exhaustion, fixation, and coloration ability of the dye on the acrylic fabric were evaluated. Using standard methods, an impartment of multifunctional effects was confirmed.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Compounds. FTIR analysis is a powerful tool for analyzing the presence of functional groups in a compound. FTIR spectra of compound I (Figure 1) revealed the presence of N−H stretching at 3423 cm^{-1}, ═C−H stretching at 3073 cm^{-1}, asymmetric C−H stretching at 2976 cm^{-1}, symmetric C−H stretching at 2874 cm^{-1}, C═O stretching at 1713 cm^{-1}, C═N stretching at 1595 cm^{-1}, and N═N stretching at 1466 cm^{-1}. Thus, the presence of various functional groups in compound I was confirmed by FTIR spectra.

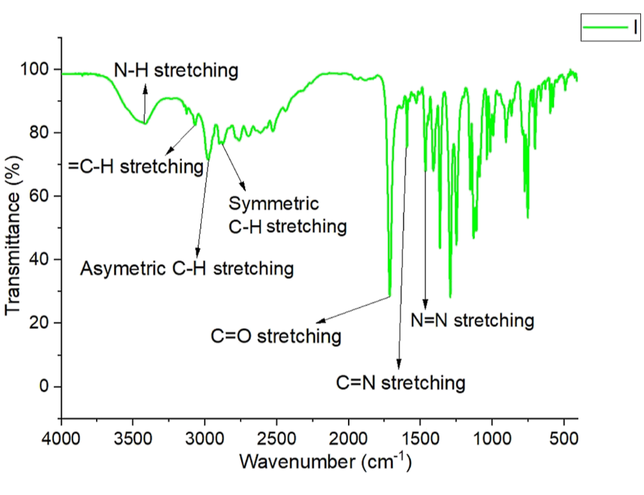

Figure 1. FTIR spectra of I.

Compound I was prepared by reacting diazotized ethyl anthranilate with imidazole. Diazotized ethyl anthranilate (an electrophile) is expected to react at the maximum electron density position of imidazole. An alkaline medium is expected to provide a good atmosphere for product synthesis. FTIR spectra previously confirmed the presence of various functional groups, and their positions of attachment were identified through NMR analysis. NMR analysis was used to analyze the chemical structure of a compound, and the presence of various protons in the synthesized compounds was identified by ^{1}H NMR. ^{1}H NMR spectra of compound I (Figure 2) showed various peaks at 1.17 ppm (a triplet with a coupling constant of 7.4 Hz) due to the methyl group, 4.27 ppm (a quartet with a coupling constant of 7.5 Hz), and 12.95 ppm (a singlet) due to NH. A multiplet due to aromatic and imidazole hydrogens was observed between 7.88 and 7.28 ppm. Thus, the chemical structure of compound I was successfully confirmed by ^{1}H NMR.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.17 (t, 3H, CH_3, J = 7.4 Hz), 4.27 (q, 2H, −CH_2, J = 7.5 Hz), 7.88−7.28 (m, 6H, Ar−H, and imidazole H), 12.95 (s, 1H, NH).

Dyes were synthesized by a coupling reaction; there is a strong chance of the traces of carbon-containing impurities, which were analyzed through ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of compound I is recorded in Figure 3. The methyl group of ester present in compound I showed a peak at 14.39 ppm, and the methylene group indicated a peak at 61.65 ppm. The imidazole and benzene ring showed peaks at 120.47, 128.36, 129.90, 130.58, 132.58, 151.61, 154.89, and 162.78 ppm. The carbon atom in the ester indicated a peak at 167.41 ppm. No impurity peaks were obtained, and the carbon NMR spectrum showed the expected outcomes for confirming the chemical structures. It concludes the synthesis of compound I.

^{13}C NMR (126 MHz, DMSO-d_6, ppm): δ = 14.39 (CH_3), 61.65 (OCH_2), 120.47, 128.36, 129.90, 130.58, 132.58, 151.61, 154.89, 162.78 (N═C−NH), 167.41 (C═O).

Figure 4 indicates the FTIR spectra of compound (II). The FTIR spectra of the dye showed N−H stretching at 3454 cm^{-1}, ═C−H stretching at 3079 cm^{-1}, C═O stretching at 1731 cm^{-1}, and N═N stretching at 1688 cm^{-1}. Hence, functional groups were confirmed by the FTIR analysis.

Figure 5 presents the ^{1}H NMR spectra of II recorded in D_2O. A triplet with a coupling constant of 7.2 Hz for the CH_3 group (attached to ester) at 1.25 ppm and a quartered due to the CH_2 group at 4.29 ppm with a coupling constant of 7.2 Hz was observed. The methyl group attached to the imidazole ring indicated a peak at 3.92 ppm as a singlet. The anionic part of the dye indicated a singlet due to the methyl group at 3.64 ppm. The aromatic hydrogens and imidazole ring hydrogens showed multiplet in the region of 7.77−7.52 ppm. Thus, proton NMR indicated the presence of all expected protons, and no other traces of reactants were obtained; the outcome successfully confirmed the chemical structure of the cationic dye.

^{1}H NMR (500 MHz, D_2O): δ = 1.25 (t, 3H, CH_3, J = 7.2 Hz), 3.64 (s, 3H, OCH_3), 3.92 (s, 3H, N−CH_3), 4.29 (q, 2H,

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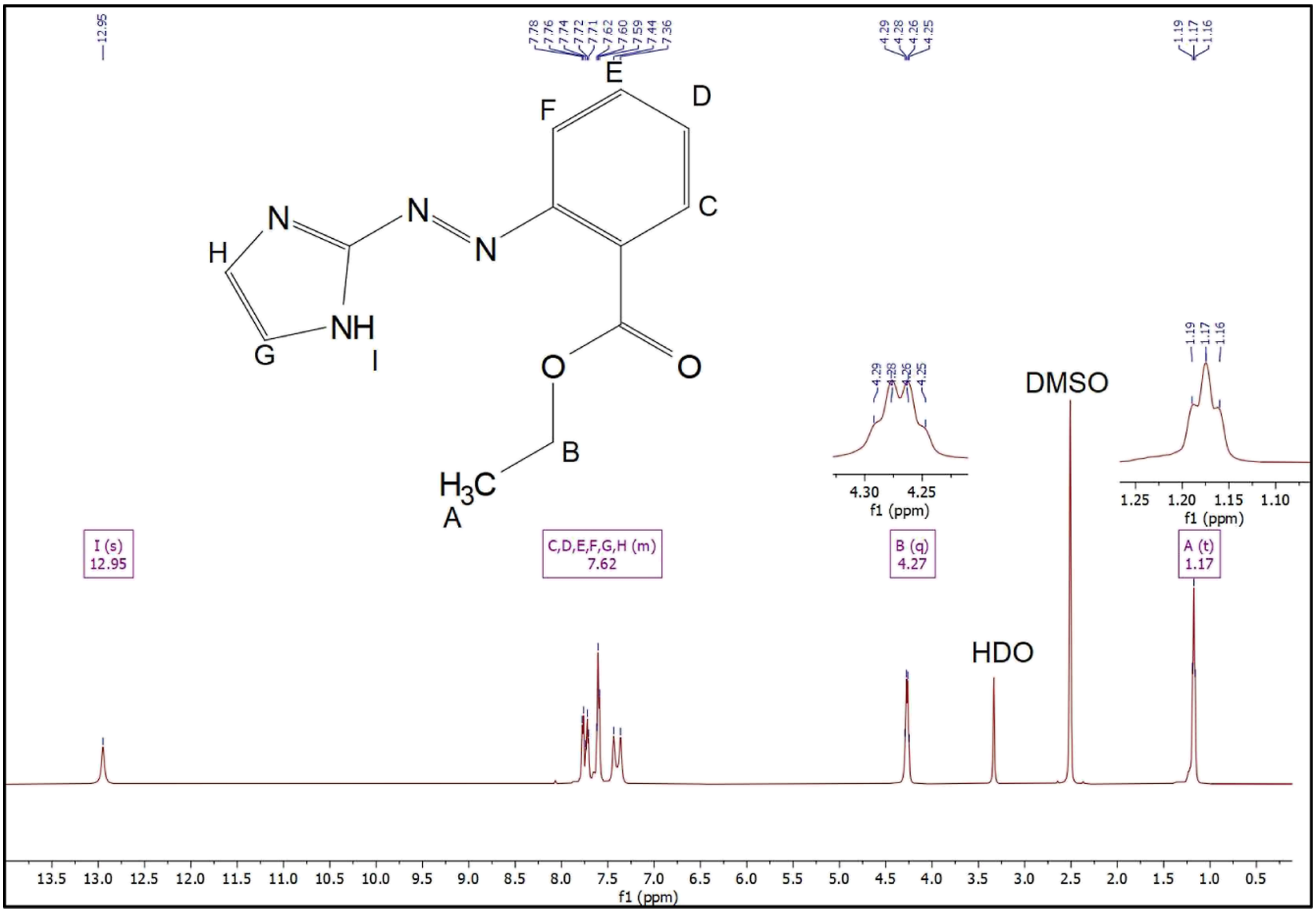

Figure 2. ^{1}H NMR spectra of I.

$-CH_2$, J = 7.2 Hz), 7.77−7.52 (m, 6H, ArH, and imidazole H).

The ^{13}C NMR spectra of II are shown in Figure 6. The methyl group showed a peak at 13.41 ppm, and the methylene group attached to the imidazole ring was observed at 36.71 ppm. The anionic part of the dye contains a methyl group which indicated a peak at 55.58 ppm. The methylene group showed a peak at 63.51 ppm. The carbon atoms due to the imidazole and benzene ring revealed peaks in the range of 116.29−161.62 ppm, respectively. The carbonyl group showed a peak at 168.77 ppm. Thus, it confirms the chemical structure of the dye.

^{13}C NMR (126 MHz, D_2O, ppm): δ = 13.41 (1C, CH_3), 36.71 (2C, N−CH_3), 55.58 (1C, OCH_3), 63.51 (1C, OCH_2), 116.29, 125.23, 129.72, 132.51, 134.67, 149.40, 161.62 (C=N), 168.77 (C=O).

The basic dye contains significant amounts of carbon, nitrogen, and hydrogen. The exact number and the positions of carbon and hydrogens were identified through NMR analysis. In order to analyze the compound for nitrogen content and nitrogen-based impurities, elemental analysis was performed.

Elemental data, molecular weight, and the IUPAC name of the dye are recorded in Table 2. The found elemental ratio was very close to the calculated values. Thus, it confirms the elemental composition of the dye.

The dissolution of the basic dye in water at different concentrations (1−5 mg/L) was performed (Figure 7). An extinction coefficient of the dye was determined from the slope of the calibration curve (Figure 7B), which indicated a value of 159.9 L g^{-1} cm^{-1}.

2.2. Color, Exhaustion, Fixation, and Fastness Analysis. Table 3 represents the color values, color strength, and appearance of the dyed fabrics. L^* values from 63 to 70, a^* values from 8 to 9, and b^* values from 40 to 41 were obtained. Color strength (K/S) was improved by increasing the shade (%). A yellow−brown shade was obtained on the fabric. Thus, the synthesized dye showed an excellent ability to impart good color strength to the acrylic fabric. Basic dyes are generally known for the brilliance of shades and high tinctorial value. The synthesized dye also confirmed the properties.

The fastness ratings of the dyed fabric are recorded in Table 4. The fastness of dyed fabrics was in the range of 4−5. A "very good" to "excellent" fastness rating suggested the wash-durable coloration effect provided by the dyed fabrics. The dye showed an exhaustion of more than 72% and a fixation of more than 80%. With increasing shade (%), a reduction in fixation and exhaustion was observed. The anionic sites are available in acrylic fabric for interaction with cationic dye molecules. Dye molecules will occupy these sites, and saturation will be reached after a certain shade (%). After the saturation point, the sites may not be available for interaction, resulting in the reduction of exhaustion and fixation at higher shade (%).

It is well established that the compounds containing anionic groups are added during the polymerization of the acrylic polymer. The presence of anionic groups makes the acrylic fiber dyeable with basic dye. The fiber becomes accessible for

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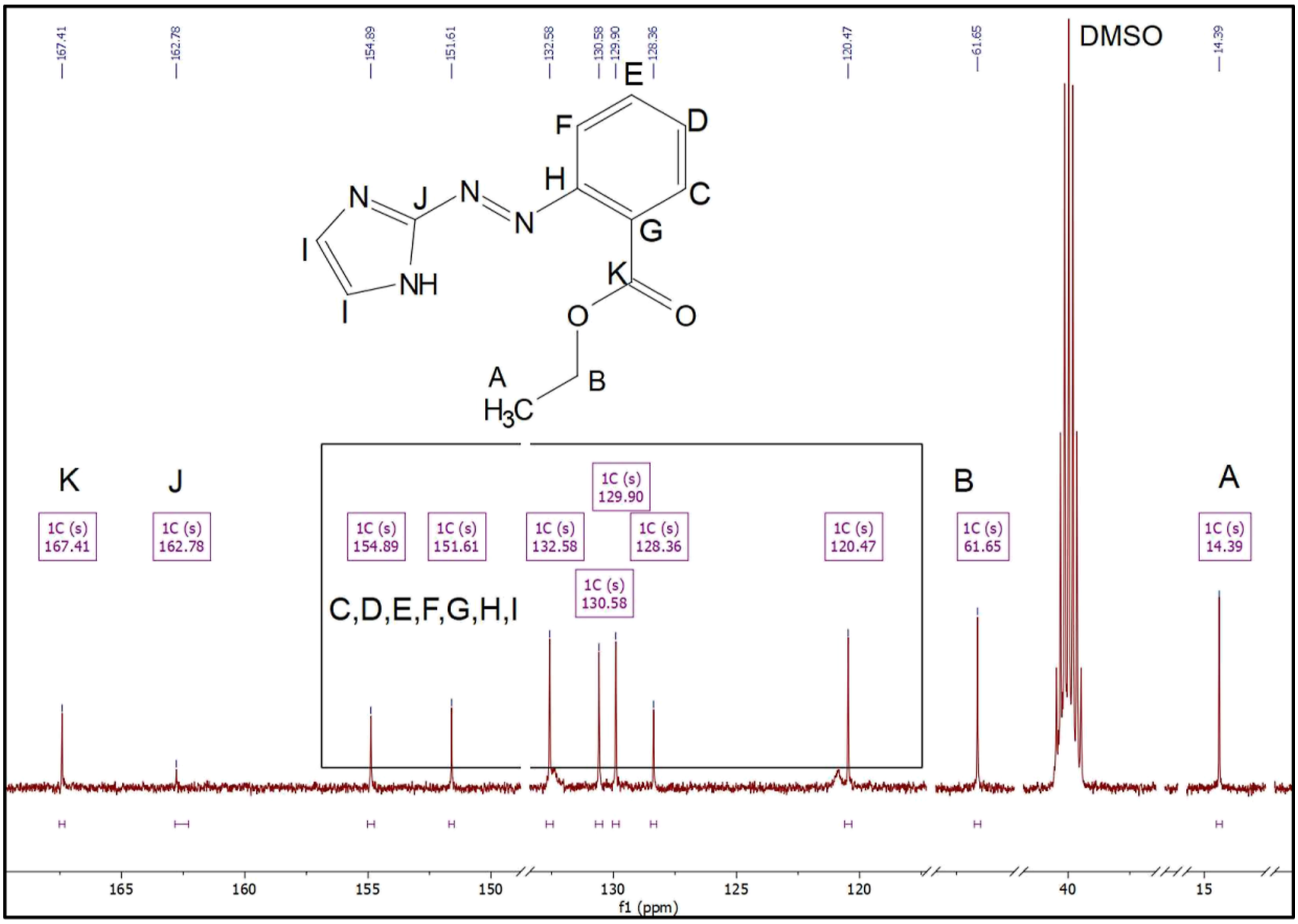

Figure 3. ^{13}C NMR spectra of I.

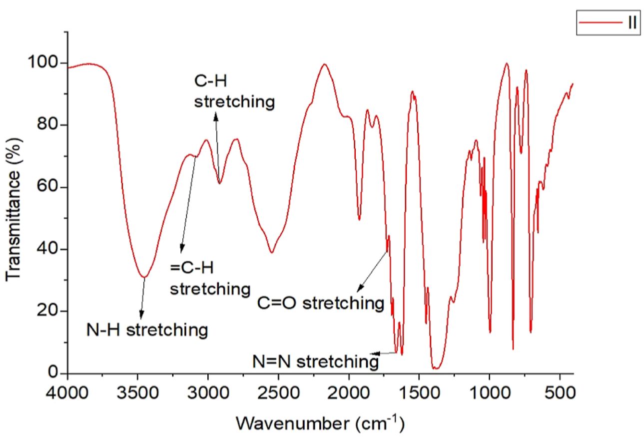

Figure 4. FTIR spectra of II.

the cationic dye's diffusion above its glass transition temperature (T_g). Figure 8 presents the interaction of the dye with the acrylic fiber. The fiber has an anionic nature, due to which it attracts the cationic dye and makes a strong electrostatic interaction. Thus, it provided satisfactory fastness; due to this, the fabric indicated wash-durable coloration effects.

2.3. Functional Properties of the Dyed Fabrics. The results of the mosquito-repellent property of dyed fabrics are recorded in Table 5. It was observed that dyed fabrics showed a repellency between 95 and 100%. The fabrics dyed with various amounts of dye on fabrics corresponding to 1, 2, 3, 4, and 5% showed a repellency of 95.12, 95.23, 97.67, 100, and 100%, respectively. The fabric dyed with a 5% shade showed a repellency of 97.72% after 20 washes. The retention of good repellency after washing treatments suggested the wash-durable repellent action imparted by the synthesized dye to the dyed fabrics. The wash-durable repellency is due to the ionic bonding between the dye and fiber, which retains the dye on the fiber after repetitive washing treatments. Thus, a modified mosquito repellent (synthesized basic dye) was confirmed as a mosquito-repellent coloring agent for acrylic fiber-based textiles.

A repellent molecule generally targets mosquitoes through contact and vapor-phase modes. A single molecule can show repellent action in both modes. In the vapor phase, repellent acts on the nervous system of the mosquitoes by evaporating itself into the atmosphere. The repellent which acts in the vapor phase can quickly go away by washing or storing the textiles for a specific period, and it may not provide a wash-durable repellency. The mosquito-repellent dye-fabric system ensures the retention of the repellent dye on the fabric as bonding/linkage retains the dye.

Contact-mode repellency is possible when mosquitoes get closer to the repellent molecule. In this case, the molecule acts as an antifeedant or an electrostatic repellent. The synthesized cationic dye interacted with the acrylic fabric through ionic linkages; such dye−fiber systems are stable against washing treatments. This enables the dyed fabric to retain the contact

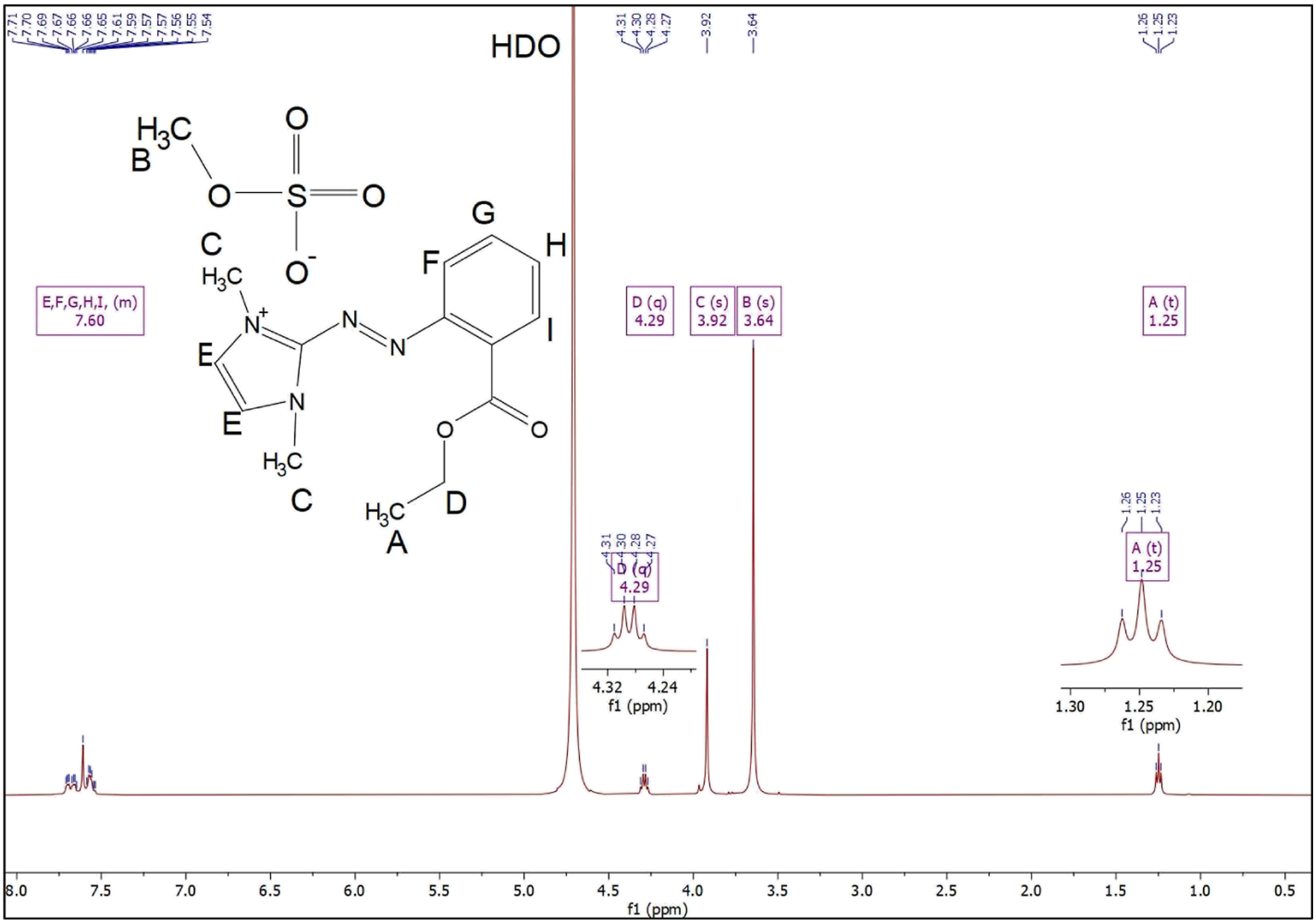

Figure 5. ^{1}H NMR spectra of II.

mode of repellency even after repetitive washings. The cationic dye contains ethyl anthranilate-repellent moiety. The acrylic fabric dyed with the repellent cationic dye imparts the mosquito repelling action through a contact-mode mechanism. The electrostatic repulsion is possible between the ester moiety of the dye and the proboscis of the mosquitoes. Such dyed fabrics can impart repellent properties till they appear colored. Figure 9 shows the mechanism of mosquito-repellent action of dyed fabrics.

The results of the UV protection property of dyed fabrics are recorded in Table 6. Good UV protection was shown by the undyed acrylic fabric. The dyed fabrics have a high UPF (UV protection factor) value and can be graded in the excellent UV protection category. UV protection provided by the dye was based on the potential of the dye to absorb UV light. A gradual improvement in UPF values with increasing shade (%) was obtained. A slight reduction in UPF values after 20 washes was observed. However, this value also lies in the excellent category. Hence, wash-durable excellent UV protection was provided to the fabric by the basic dye.

The dye is a UV-absorbing molecule because it possesses electronic transition properties, as confirmed through UV–vis spectroscopy. The undyed fabric easily allows the transmission of UV rays. The dyed fabric absorbs the UV rays due to the UV-absorption ability of the dye which prevents the rays from passing through the fabric, thereby providing excellent UV protection. With upgrading shade (%), the amount of the dye on the fabric gets increased, and it promotes the absorption of more UV rays, thus improving the UPF value. Some of the dye molecules get washed away due to abrasive washing treatments, thus reducing the UPF value.

2.4. Thermogravimetric Analysis and X-ray Diffraction Analysis of Fabrics. The thermal stability of undyed and dyed acrylic fabrics was evaluated, and the results are recorded in Figure 10A. The curve of weight (%) against temperature suggested insignificant changes in the thermal stability of the acrylic fabric after dyeing. The transition temperatures, such as T_{10} (temperature of 10% weight loss), T_{25}, and T_{50}, are recorded in Table 7. The difference between these transition temperatures was insignificant. Thus, the thermal stability of the fabric was not affected after dyeing.

In order to analyze the change in the crystalline nature of the fiber after dyeing, X-ray diffraction (XRD) analysis was carried out. The XRD pattern of the fabrics is recorded in Figure 10B. The crystalline peaks at $2\theta = 17°$ and $2\theta = 29.3°$ were due to the crystalline plane (100) and (110).[55] The undyed and dyed fabrics showed a similar XRD pattern. The intensity of the (100) crystalline peak at 17° was reduced after dyeing. This suggested a reduction in the crystallinity of acrylic fiber after the dyeing. The application of dye to acrylic fabric causes hydrolysis of the fiber and reduces its crystalline nature. Moreover, interaction with the cationic dye with the fabric can also promote the reduction in the crystallinity.

2.5. Tensile Strength of the Fabrics. The undyed fabric showed a tensile strength of 422.67 N (average of three replicates), and the dyed fabric (5% shade) showed a tensile

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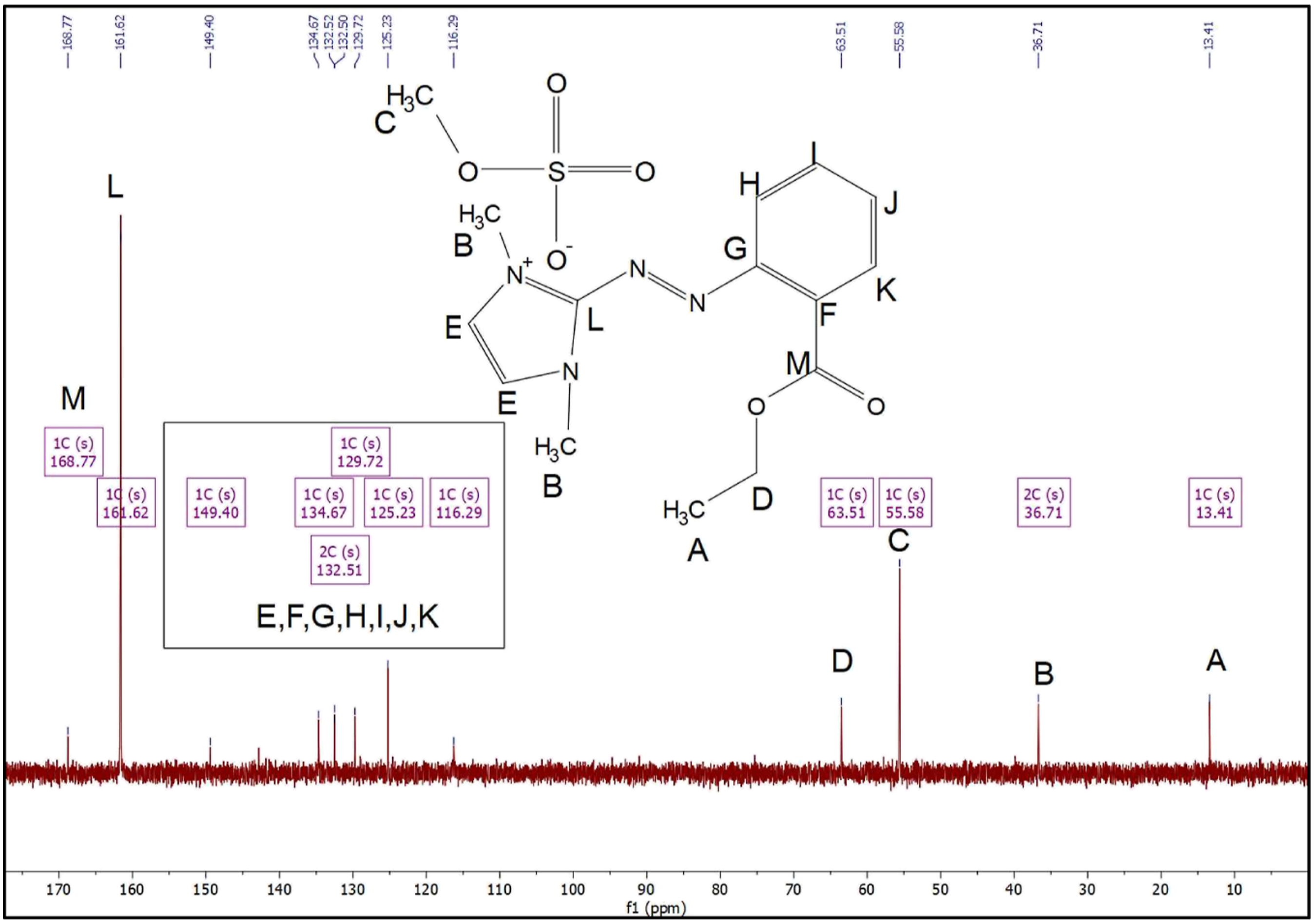

Figure 6. ^{13}C NMR spectra of II.

Table 2. Elemental Analysis of the Dye

molecular formula	molecular weight	IUPAC name	% C found (calculated)	% H found (calculated)	% N found (calculated)
$C_{15}H_{20}N_4O_6S$	384.41	2-{(*E*)-[2-(ethoxycarbonyl)phenyl]diazenyl}-1,3-dimethyl-1*H*-imidazol-3-ium methyl sulfate	46.34 (46.87)	5.13 (5.24)	14.02 (14.57)

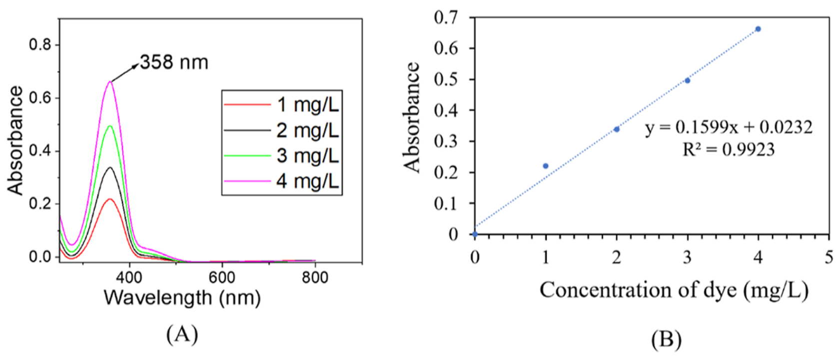

Figure 7. (A) UV−vis spectra of the dye; (B) calibration curve of the dye.

strength of 321.07 N (average of three replicates). A reduction in the tensile strength of 24.04% was observed after the dyeing. The reduction in the strength is due to the hydrolysis of the fiber at the dyeing temperature. Also, the interaction of the dye with the fiber promotes the loss of tensile strength. The conventional method is used for the dyeing of the fabric, which is already an industrial procedure for the dyeing of acrylic fabrics.

3. CONCLUSIONS

A novel mosquito-repellent basic dye based on ethyl anthranilate mosquito repellent was prepared. Synthesis of the reported cationic dye involves the reaction of the

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Table 3. Color Analysis of the Dyed Fabrics

Shade (%)	Color values[a]			Color strength[a]	Color appearance
	L*	a*	b*	K/S	
1	70.339	8.665	40.443	3.681	
2	66.606	8.904	40.038	4.673	
3	66.621	9.729	41.583	5.057	
4	63.899	9.775	40.82	5.892	
5	63.231	9.760	40.693	6.074	

[a]Represents the average value of three determinations.

Table 4. Exhaustion and Fixation of the Dye on Acrylic Fabric and Fastness Properties of the Dyed Fabric

shade (%)	washing fastness	rubbing fastness		light fastness	exhaustion (%)	fixation (%)
		dry	wet			
1	5	5	4−5	4−5	90.32	95.65
2	5	5	4−5	4−5	85.42	92.64
3	4−5	5	4−5	5	83.57	88.54
4	4−5	4−5	4−5	5	78.41	84.76
5	4−5	4	4−5	5	72.96	80.58

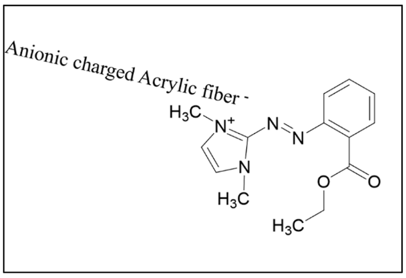

Figure 8. Mechanism of the interaction of the dye with fiber.

Table 5. Mosquito Repellency of Dyed Fabrics

shade (%)	mosquito repellency (%)[a]
1	95.12
2	95.23
3	97.67
4	100
5	100
5% shade polyester after 20 washes	97.72

[a]Represents the average value of three determinations.

diazotized product of ethyl anthranilate with imidazole, followed by quaternization. The dye was applied to the acrylic fabric using the conventional dyeing method to generate strong coloration and fastness effects. The coloration properties of dyed fabrics (L^*, a^*, b^*, K/S) were additionally examined, and $K/S > 3$ was obtained. Exhaustion > 72% and fixation >80% confirmed the suitability of the dye for acrylic fabric dyeing. 100% mosquito-repellent and excellent UV protection properties by the dyed acrylic fabric were successfully obtained. Thermogravimetric analysis (TGA) analysis also suggested an insignificant change in thermal stability due to the application of the dye to the acrylic fabric. XRD analysis suggested a reduction in crystalline peak intensity after the dyeing. The wash durability was obtained for both mosquito-repellent and UV-protective functionalities of dyed fabrics. The multifunctional acrylic fabric can be used to prepare technical textiles, home textiles, and apparel textiles. The developed dye has cationic nature, and it can also be explored for the coloration of wool and nylon fibers.

4. EXPERIMENTAL SECTION

4.1. Materials. Ethyl anthranilate, sodium nitrite, hydrochloric acid (36%), imidazole, dimethyl sulfate, and acetone were purchased from TCI (Tokyo Chemical Industry). Ready-for-dyeing, 100% acrylic fabric (EPI = 44, PPI = 37, GSM = 150) was used in the experiments.

4.2. Preparation of I [Ethyl (*E*)-2-((1*H*-imidazole-2-yl)diazenyl)benzoate]. Ethyl anthranilate (0.04 mol, 6.60 g) was stirred with 8.6 mL of hydrochloric acid (36%) in 80 mL of water. 2.75 g (0.04 mol) of sodium nitrite ($NaNO_2$) was reacted with the reaction mixture at 0−5 °C for 4−5 h. The diazonium salt solution with a pH of 5−6 was obtained by neutralization with sodium acetate.

0.04 mol (2.72 g) of imidazole was dissolved in 100 mL of water. The diazotized solution of ethyl anthranilate was added dropwise to the imidazole solution with a maintained pH of 8−9. The product was obtained after filtration and several washing steps with hot water and hexane. The final product was collected after drying in a vacuum oven. The reaction scheme and appearance of the product are depicted in Figure 11.

4.3. Preparation of II [(*E*)-2-((2-(Ethoxycarbonyl)-phenyl)diazenyl)-1,3-dimethyl-1*H*-imidazole-3-ium] (Basic Dye). A fine powder of 0.0123 mol (4 g) of I in 50 mL of water was added to a three-necked flask. Dimethyl sulfate (0.0656 mol, 8.28 g) was added slowly to the flask for 30 min. Quaternization was done for 2 h at 60 °C (as per thin-layer chromatography progress). Acetone was added to the mixture to precipitate out the dye. The precipitated dye was filtered, washed with acetone, and dried to get product II.

4.4. Characterization of Compounds and Acrylic Fabrics. The compounds were characterized for the functional group using Fourier-transform infrared (FTIR) spectroscopy. The structural characterization of the compounds was done by ^{1}H NMR and ^{13}C NMR. The UV−vis spectra of the basic dye in deionized water were analyzed using a UV−vis spectrophotometer (UV-1900i, Shimadzu). An elemental analyzer (PerkinElmer) was utilized for analyzing the dye's elemental composition (C, H, and N). The dyed fabrics were characterized for thermal stability (TGA) under a N_2 atmosphere at 20 °C/min. The fabrics were also characterized by the XRD technique using X'Pert PRO (PANalytical Netherlands). TGA (PerkinElmer) of fabrics was also done in the temperature range of 50−800 °C and a heating rate of 20 °C/min under a N_2 atmosphere.

4.5. Dyeing of Acrylic Fabrics. The dyeing of acrylic fabrics was carried out in an infrared dyeing machine at different shade % (1, 2, 3, 4, and 5). The dyeing was performed at 95 °C for 1 h at a pH of 3−4. A cold washing of dyed fabrics followed by hot washing was performed. Air drying was done to obtain the final dyed fabric.

4.6. Color, Exhaustion, and Fixation Measurements. The dyed fabric was evaluated for color values (L^*, a^*, and b^*) and color strength (K/S) using a computer color-matching machine (Premier Colorscan, SS5100H).

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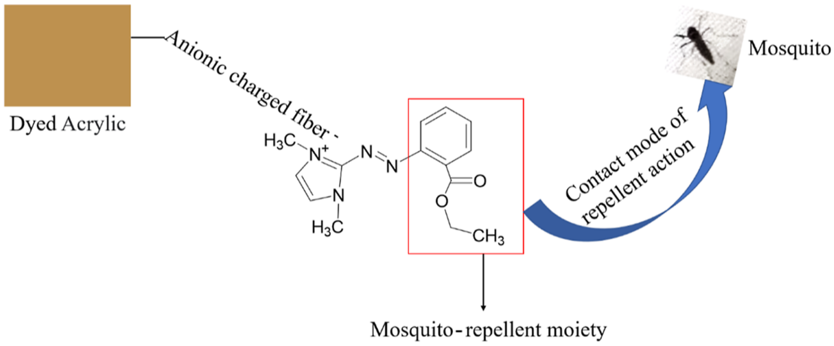

Figure 9. Mechanism of dyed acrylic for mosquito-repellent protection.

Table 6. UV Protection Offered by Acrylic Fabrics

sample	UV protection factor value ±standard deviation	UV protection rating
undyed acrylic	18.72 ± 0.98	good
1% shade	121.39 ± 0.45	excellent
2% shade	151.58 ± 0.13	excellent
3% shade	272.95 ± 1.35	excellent
3% shade after 20 washes	190.32 ± 0.25	excellent

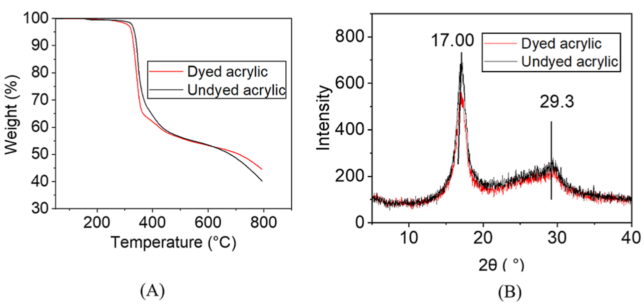

Figure 10. (A) TGA of the fabrics; (B) XRD analysis of the fabrics.

Table 7. Thermal Transition Temperatures of Fabrics

sample name	T_{10}	T_{25}	T_{50}
undyed acrylic	342	356	679
dyed acrylic	331	346	710

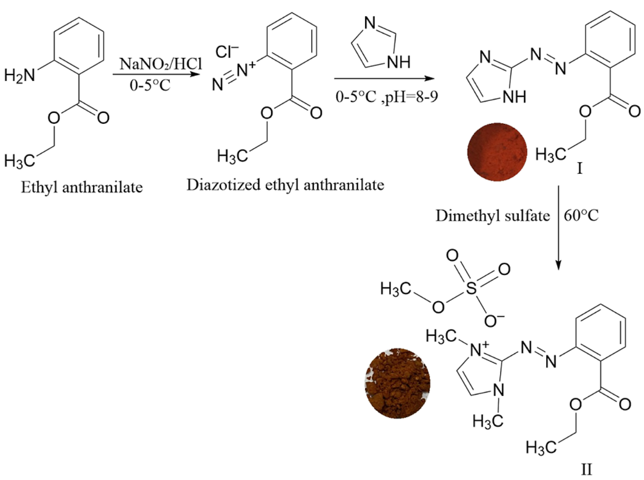

Figure 11. Preparation of the basic dye.

Equations 1 and 2 were used to calculate exhaustion and fixation values, respectively

$$\text{exhaustion (\%)} = (A_b - A_a)/A_b \times 100 \quad (1)$$

where A_b = absorbance value of dye liquor before dyeing and A_a = absorbance value of dye liquor after dyeing

$$\text{fixation (\%)} = \frac{\left(\frac{K}{S}\text{ value just after dyeing} - \frac{K}{S}\text{ value of dyed fabric after washing}\right)}{\frac{K}{S}\text{ value just after dyeing}} \times 100 \quad (2)$$

4.7. Fastness and Functional Property Evaluation of Dyed Fabrics. ISO 105-C06, ISO 105-X12, and ISO 105 BO2 methods[56] were utilized to assess the washing fastness, rubbing fastness, and lightfastness of the dyed fabrics, respectively. Mosquito-repellent properties and UV protection of dyed fabrics were analyzed according to "Arm in cage"[9] and AS/NZS 4399 (1996),[57] respectively.

To evaluate the mosquito-repellent properties of the dyed fabric, Anopheles female mosquitoes were transferred to a cage. A user wrapped both fabrics (undyed and dyed) on his arm and put them in the cage. The repellent properties (repellency) were calculated using the following formula, and an average of three replicates was recorded.

$$\text{Mosquito repellency \%} = [(M - N)/N] \times 100$$

where M = number of mosquitoes that landed on the undyed acrylic fabric and N = number of mosquitoes that landed on the dyed acrylic fabric.

4.8. Laundering Treatments of Dyed Fabrics. To assess the functional properties against laundering treatments, the standard method AATCC-61A was utilized.[58] The dyed fabric, a standard detergent solution, and steel balls were loaded in a launderometer, and washing was performed at 40 °C for 45 min. Similar experiments were repeated with a freshly prepared detergent solution for the second washing cycle, which was continued.

4.9. Evaluation of Tensile Strength of Fabrics. The standard method, "ASTM D 5035 (1995)", was utilized for the determination of the tensile strength of the fabrics.[59]

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Notes

The authors declare no competing financial interest.

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