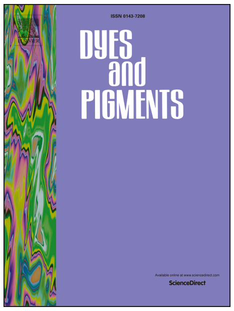

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Microwave-assisted synthesis and photochromic properties of new azo-imidazoles

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Abstract

A convenient, one-pot three-component synthesis of new photochromic azo-imidazoles (**1a-1h**) from the corresponding azo dyes (**2a-2h)**, benzil and ammonium acetate under microwave irradiation were described and their photochromic properties were investigated. The structures of the new azo-imidazoles were confirmed by UV-Vis, FT-IR and NMR spectroscopies and elemental analysis. The properties and photochromic structural behavior relationship (PSBR) of these compounds have been analyzed. All the compounds exhibit good photochromic behavior upon irradiation with alternative UV and visible light.

Keywords: Azo-imidazole, Azo dyes, Imidazole, Microwave, Photochromism.

1. Introduction

Photochromic compounds have attracted considerable attention due to their extensive application in display and anti-counterfeiting systems, optical storage and memory devices, and optical molecular switches [1–9]. Hence, in the past decade, a large number of photochromic compounds with different photoresponsive units have been synthesized and their properties have been investigated [10–13]. Azo dyes are an important and large class of synthetic organic colorants used in many practical applications [14,15]. The photochromism and thermochromism of aromatic azo dyes make them suitable as optical sensors, nonlinear optical chromophores and molecular memory storage [16–20]. A representative family of azobenzenes photochromic molecules, induced by alternating irradiation with ultraviolet and

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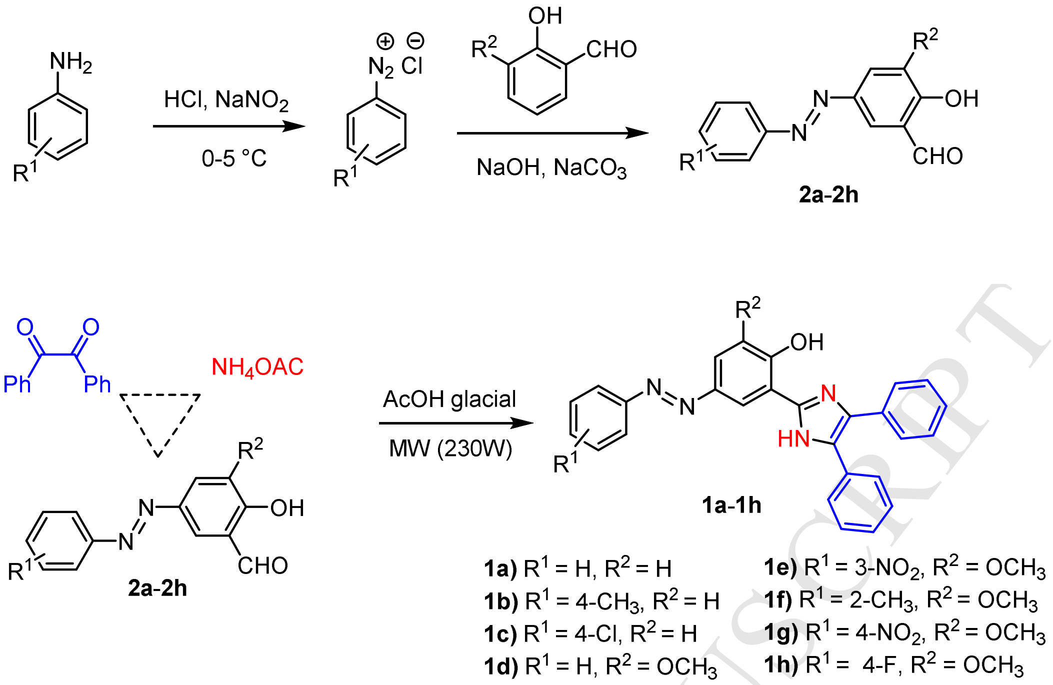
blue lights, conducting *E* to *Z* and vice versa photoisomerization via azo π–π^* and azo n–π^* excitations, respectively [21]. Regarding synthesis of heterocyclic azo dyes with thiophene, pyrrole and azoles, several reports recently have been published. These azo dyes were used as optical switching, second harmonic generation, chemo-sensing, organic sensitized solar cells and memories [22–24].

The imidazole unit is a key building block that has been widely used in medicine, ionic liquids, anion sensors, as well as electronic and optical materials [25–29]. Hence, it convinces us to incorporate an imidazole unit into an azo dye, it is anticipated that the azo-imidazoles with excellent photochromic properties will be obtained.

Because of the advantages of short reaction time, high efficiency, improving reaction yields, and reducing thermal degradation byproducts, microwave-assisted synthesis has been successfully and routinely applied in organic and medicinal chemistry [30-33]. In continuation of our interest in the development of photochromic compounds [34–39] here, for the first time we report the coupling of the photoactive azo aldehydes (**2a**-**2h**), benzil and NH_4OAc in convenient, one-pot three-component synthesis under microwave irradiation to azo-imidazoles (Scheme 1) and investigate their PSBR. The results indicate that upon irradiation of **1a**-**1h** with UV/Vis light they can be easily isomerized to their corresponding photoisomers.



Scheme 1. General synthetic route for synthesis of azo-imidazoles

2. Experimental

2.1. Materials and apparatus

All reagents were purchased from Fluka, Merck and Aldrich and used without further purification. Azo dyes precursors, **2a-2h**, were prepared according to the well-known literature procedure [40]. Melting points were measured by electrothermal 9100s apparatus and were uncorrected. FT-IR spectra were recorded on a Bruker Vecter 22 in the region of 400–4000 cm^{-1} in KBr pellets. The ^{1}HNMR and ^{13}C NMR spectra were obtained from solution DMSO-d_6 and $CDCl_3$ with TMS as an internal standard Bruker Avance III (400 MHz) spectrometer. The absorption spectra of azo-imidazoles were measured by Shimadzu UV-2100 spectrophotometer in the range 200–800 nm ($c = 2 \times 10^{-4}$ M, cell path length 1 cm). Spectral data were obtained using quartz cuvettes with 1 cm optical path length before and after UV irradiation for various times. A light at 254 nm from a low-pressure Hg lamp was used for the photoisomerization from the trans-enol photoisomer to the cis-keto photoisomer. The CHN analyses were performed on a Vario-ELIII elemental analyzer. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95, EI: 70 eV, R:10000. Microwave-assisted reactions were carried out on a commercially available monomode microwave unit (CEM Discover) in a 25-mL round-bottom flask. The machine consists of a continuous focused microwave power delivery system with operator selectable power output from 0 to 300 W. Reactions were performed in a 25-mL round-bottom flask. The temperature of the contents of the vessel was monitored using an IR sensor located underneath the reaction vessel. Primary microwave irradiation of 230 W was used, the temperature being ramped from rt to reflux.

2.2 Synthesis

*2.2.1. General procedure for the synthesis of azo-imidazoles **1a-1h***

Azo day **2a-2h** (1 mmol), benzil (0.210 g, 1 mmol) and NH_4OAc (0.310 g, 4 mmol) in AcOH glacial (4 ml) were heated in a stirred microwave open-vessel (230 W) for appropriate time 1.5-2.5 min see Table 2. The progress of the reaction was monitored by TLC (eluent: *n*-hexane:EtOAc, 6:2). After completion of the reaction distilled H_2O was added to the mixture and the precipitated solid was collected by filtration, and recrystallized from EtOH or EtOH/$CHCl_3$ to give azo-imidazoles **1a-1h** in high yields 82-96% see Table 2.

2.3. Spectral data for the synthesis of azo-imidazoles

*2.3.1. 2-(4,5-Diphenyl-1H-imidazol-2-yl)-4-(phenyldiazenyl)phenol (**1a**)*

Yield: 87%, mp 191-192 °C, orange crystal; FT-IR (KBr, υ/cm^{-1}): 3059 (aromatic C–H stretch), 1603 (C=N stretch), 1496 (N=N stretch), 1439, 1383, 1269 (C–O stretch), 767, 693 (aromatic out of plane bend). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.20 (d, J = 8.8 Hz, 1H), 7.45 (br, 6H), 7.54-7.64 (m, 7H), 7.87-7.92 (m, 3H), 8.79 (d, J = 2.4 Hz, 1H), 13.46 (br, 1H), 13.79 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 113.7, 118.4, 121.8, 122.6, 124.3, 126.9-129.7

(br, 3 arom C), 127.9, 129.2, 129.9, 131.3, 145.5, 145.6, 152.6 and 160.3. Anal. Calcd. For $C_{27}H_{20}N_4O$: C, 77.87; H, 4.84; N, 13.45%. Found: C, 77.91; H, 4.92; N, 13.43%. HRMS: *m*/*z* for $C_{27}H_{20}N_4O$; calculated 416.1574; found: 416.1576.

*2.3.2. 2-(4,5-Diphenyl-1H-imidazol-2-yl)-4-(p-tolyldiazenyl)phenol (**1b**)*

Yield: 88%, mp 198-200 °C, orange powder; FT-IR (KBr, υ/cm^{-1}): 3236 (N–H stretch), 3029 (aromatic C–H stretch), 1598 (C=N stretch), 1491 (N=N stretch), 1440, 1383, 1278 (C–O stretch), 825, 764, 694 (aromatic out of plane bend). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.43 (s, 3H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 4H), 7.43 (br, 5H), 7.58 (d, *J* = 7.2 Hz, 4H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.76 (d, *J* = 2.4 Hz, 1H), 13.40 (br, 1H), 13.73 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 21.5, 113.7, 118.3, 121.7, 122.7, 124.0, 127-129.5 (br, 2 arom C), 127.5, 128.2, 129.1, 130.4, 141.4, 145.6, 145.7, 150.7 and 160.1. Anal. Calcd. For $C_{28}H_{22}N_4O$: C, 78.12; H, 5.15; N, 13.01%. Found: C, 78.17; H, 5.21; N, 12.97%. HRMS: *m*/*z* for $C_{28}H_{22}N_4O$; calculated 430.1781; found: 430.1786.

*2.3.3. 4-((4-Chlorophenyl) diazenyl)-2-(4, 5-diphenyl-1H-imidazol-2-yl)phenol (**1c**)*

Yield: 82%, mp 215-217 °C, dark orange crystal; FT-IR (KBr, υ/cm^{-1}): 1605 (C=N stretch), 1490 (N=N stretch), 1441, 1384, 1274 (C–O stretch), 832, 766, 694 (aromatic out of plane bend). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.20 (d, *J* = 8.8 Hz, 2H), 7.41-7.45 (br, 6H), 7.57 (d, *J* = 7.2 Hz, 4H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.88-7.91 (m, 3H), 8.78 (d, *J* = 2.4 Hz, 1H), 13.56 (br, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 113.8, 118.4, 121.7, 124.3, 124.5, 127.5-129 (br, 3 arom C), 128.3, 129.2, 130.1, 135.6, 145.4, 145.5, 151.2 and 160.6. Anal. Calcd. For $C_{27}H_{19}N_4OCl$: C, 71.92; H, 4.25; N, 12.43%. Found: C, 71.88; H, 4.21; N, 12.47%. HRMS: *m*/*z* for $C_{27}H_{19}ClN_4O$; calculated 450.1209; found: 450.1214.

*2.3.4. 2-(4,5-Diphenyl-1H-imidazol-2-yl)-6-methoxy-4-(phenyldiazenyl)phenol (**1d**)*

Yield: 88%, mp 232-234 °C, golden crystal; FT-IR (KBr, υ/cm^{-1}): 3056 (aromatic C–H stretch), 1602 (C=N stretch), 1471 (N=N stretch), 1390, 1267 (C–O stretch), 762, 692 (aromatic out of plane bend). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 3.96 (s, 3H), 7.41(br, 2H), 7.46 (t, J = 7.2 Hz, 4H), 7.54 (d, J = 2.0 Hz, 1H), 7.55-7.64 (m, 7H),7.90 (d, J = 7.2 Hz, 2H), 8.51 (d, J = 2.0 Hz, 1H), 13.55 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 56.3, 104.1, 112.2, 113.9, 122.6, 127-129.3 (br, 4 arom C), 127.7, 128.8, 129.2, 130.6, 145.1, 149.8, 150.7 and 152.6. Anal. Calcd. For $C_{28}H_{22}N_4O_2$: C, 75.32; H, 4.97; N, 12.55%. Found: C, 75.38; H, 5.01; N, 12.51%. HRMS: m/z for $C_{28}H_{22}N_4O_2$; calculated 446.1692; found: 416.1695.

*2.3.5. 2-(4,5-Diphenyl-1H-imidazol-2-yl)-6-methoxy-4-((3-nitrophenyl)diazenyl)phenol (**1e**)*

Yield: 96%, mp 248-250 °C, golden crystal; FT-IR (KBr, υ/cm^{-1}): 1622 (C=N stretch), 1522 (NO_2 asymmetric stretch), 1463, 1386, 1345 (NO_2 symmetric stretch), 1273 (C–O stretch), ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 3.97 (s, 3H), 7.40 (t, J = 7.4 Hz, 2H), 7.47 (t, J = 7.4 Hz, 4H), 7.58-7.60 (m, 5H), 7.94 (t, J = 8.0 Hz, 1H), 8.39 (t, J = 7.8 Hz, 2H), 8.59 (d, J = 2.0 Hz, 1H), 8.63 (d, J = 1.6 Hz, 1H). Anal. Calcd. For $C_{28}H_{21}N_5O_4$: C, 68.42; H, 4.31; N, 14.25%. Found: C, 68.38; H, 4.29; N, 14.23%. HRMS: m/z for $C_{28}H_{21}N_5O_4$; calculated 491.1624; found: 491.1627.

*2.3.6. 2-(4,5-Diphenyl-1H-imidazol-2-yl)-6-methoxy-4-(o-tolyldiazenyl)phenol (**1f**)*

Yield: 95%, mp 277-278 °C, orange-red crystal; FT-IR (KBr, υ/cm^{-1}): 3286 (N–H stretch), 3058 (aromatic C–H stretch), 1603 (C=N stretch), 1478 (N=N stretch), 1450, 1388, 1274 (C–O stretch), 849, 759, 696 (aromatic out of plane bend). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.73 (s, 3H), 3.95 (s, 3H), 7.33-7.46 (br m, 9H), 7.52 (d, J = 2.0 Hz, 1H), 7.58 (d, J = 6.8 Hz, 5H), 8.50 (d, J = 2.0 Hz, 1H), 13.48 (br, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 17.7, 56.1, 102.3, 113.0, 115.5, 117.9, 126.5-129.5 (br, 3 arom C), 127.1, 128.3, 129.1, 131.0, 131.9, 137.5, 145.5, 145.8, 149.8, 150.5 and 150.8. Anal. Calcd. For $C_{29}H_{24}N_4O_2$: C, 75.63; H, 5.25; N, 12.17%. Found: C, 75.68; H, 5.30; N, 12.14%. HRMS: m/z for $C_{29}H_{24}N_4O_2$; calculated 460.1884; found: 460.1889.

*2.3.7. 2-(4,5-Diphenyl-1H-imidazol-2-yl)-6-methoxy-4-((4-nitrophenyl)diazenyl)phenol (**1g**)*

Yield: 96%, mp 250-251 °C, dark red crystal; FT-IR (KBr, υ/cm^{-1}): 1615 (C=N stretch), 1515 (NO_2 asymmetric stretch), 1384, 1336 (NO_2 symmetric stretch), 1251 (C–O stretch), 852, 764, 693 (aromatic out of plane bend). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 3.97 (s, 3H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 4H), 7.57-7.59 (m, 5H), 8.07 (d, *J* = 8.8 Hz, 2H), 8.47 (d, *J* = 9.2 Hz, 2H), 8.61 (s, 1H), 13.84 (br, 2H). Anal. Calcd. For $C_{28}H_{21}N_5O_4$: C, 68.42; H, 4.31; N, 14.25%. Found: C, 68.47; H, 4.42; N, 14.28%. HRMS: *m*/*z* for $C_{28}H_{21}N_5O_4$; calculated 491.1624; found: 491.1626.

*2.3.8. 2-(4,5-Diphenyl-1H-imidazol-2-yl)-4-((4-fluorophenyl)diazenyl)-6-methoxyphenol (**1h**)*

Yield: 92%, mp 230-232 °C, golden crystal; FT-IR (KBr, υ/cm^{-1}): 1599 (C=N stretch), 1465, 1387, 1271 (C–O stretch), 842, 766, 695 (aromatic out of plane bend). ^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ (ppm): 3.95 (s, 3H), 7.41 (br, 2H), 7.43-7.48 (m, 6H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 4H), 7.96 (dd, *J* = 9.0, 5.4 Hz, 2H), 8.49 (d, *J* = 2.0 Hz, 1H), 13.61 (br, 2H). ^{13}C NMR (100 MHz, DMSO-*d$_6$*) δ (ppm): 56.3, 102.4, 102.8, 113.1, 116.8, 117.0, 117.4, 124.8, 124.9, 128.3, 127.5-129.5 (br, 1 arom C), 129.2, 144.8, 145.8, 149.3, 149.9 and 162.6. Anal. Calcd. For $C_{28}H_{21}N_4O_2F$: C, 72.40; H, 4.56; N, 12.06%. Found: C, 72.47; H, 4.61; N, 12.05%. HRMS: *m*/*z* for $C_{28}H_{21}FN_4O_2$; calculated 464.1593; found: 464.1599.

3. Results and discussion

In continuation to our prior works [34–39], herein, *o*-vanillin or salicylaldehyde in the first step was coupled with the diazonium chloride obtained from aniline derivatives to give azo dyes **2a-2h**. In the next efforts, the azo-imidazoles **1a-1h** were synthesized via three-component reactions between benzil, NH_4OAc and azo dye precursor under microwave irradiation in the presence of AcOH glacial as solvent and organocatalyst in short reaction times, as shown in Scheme 1 and Table 2. The prepared azo-imidazoles **1a-1h** exhibited photoisomerization conversion in the $CHCl_3$ solution.

To optimize reaction condition for the synthesis of azo-imidazoles, the one-pot three-component reaction of azo dye **2a** (1 mmol), benzil (1 mmol) and NH_4OAc (4 mmol) was selected as the model reaction. Using different types of catalysts e.g. under reflux (entries 1-6 in Table 1) and microwave (entry 7 in Table 1) conditions the reaction proceeded slowly. When reaction performed in the presence of AcOH glacial as the solvent and catalyst under reflux condition afforded the azo-imidazole **1a** in good yield (Entry 8). When the reaction was run in the presence of AcOH glacial under microwave irradiation the best result was obtained (entry 9). The goal of a reaction optimization is to select the best inputs to achieve, a shorter reaction time, high yield and simple workup procedure as shown in entry 9.

Table 1. Optimization of the synthesis of **1a**

Entry	Solvent	Catalyst (10 mol%)	Condition	Time (min)	Yield%
1	EtOH	$ZnCl_2$	Reflux	720	15
2	EtOH	KSF	Reflux	720	44
3	EtOH	KSF@Zn	Reflux	720	30
4	$CHCl_3$	KSF@Zn	Reflux	720	40
6	EtOH	*p*-TSA	Reflux	720	10
7	EtOH	$NiCl_2$	MW (230W)	30	10
8	AcOH	-	Reflux	360	82
9	**AcOH**	**-**	**MW (230W)**	**2**	**87**

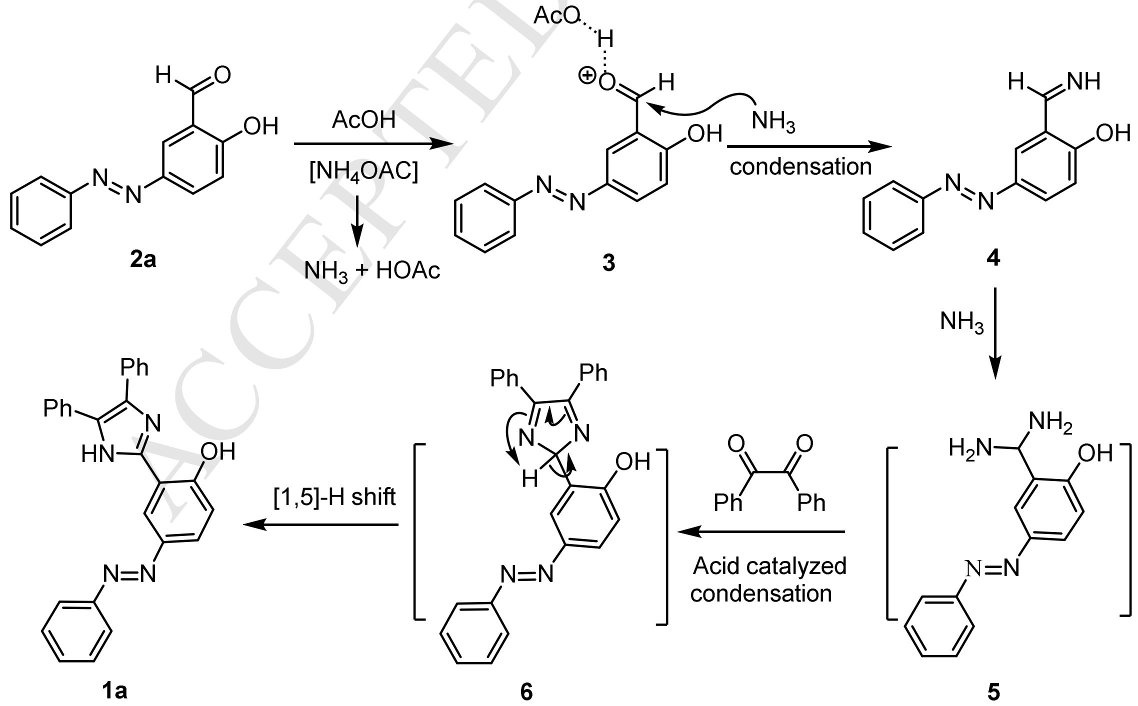
In order to evaluate the generality of the process, different azo dyes **2a**-**2h** were used in the synthesis of azo-imidazoles **1a**-**1h** under optimized reaction condition (Table 2). As shown, in Table 2 the expected products were obtained in short reaction time (1.5–2.5 min) with high yields without formation of any byproducts. The structures of prepared compounds were confirmed by analyzing their spectral characteristics.

The FT-IR spectra of **1a**-**1h** indicate the absence of C=O stretching vibration of azo aldehyde precursors **2a**-**2h** and benzil and appearance of a new C=N absorption band in the range of 1598-1622 cm^{-1} confirm the formation of imidazole ring.

Table 2. Microwave-assisted synthetic of photochromic azo-imidazoles **1a**-**1h**

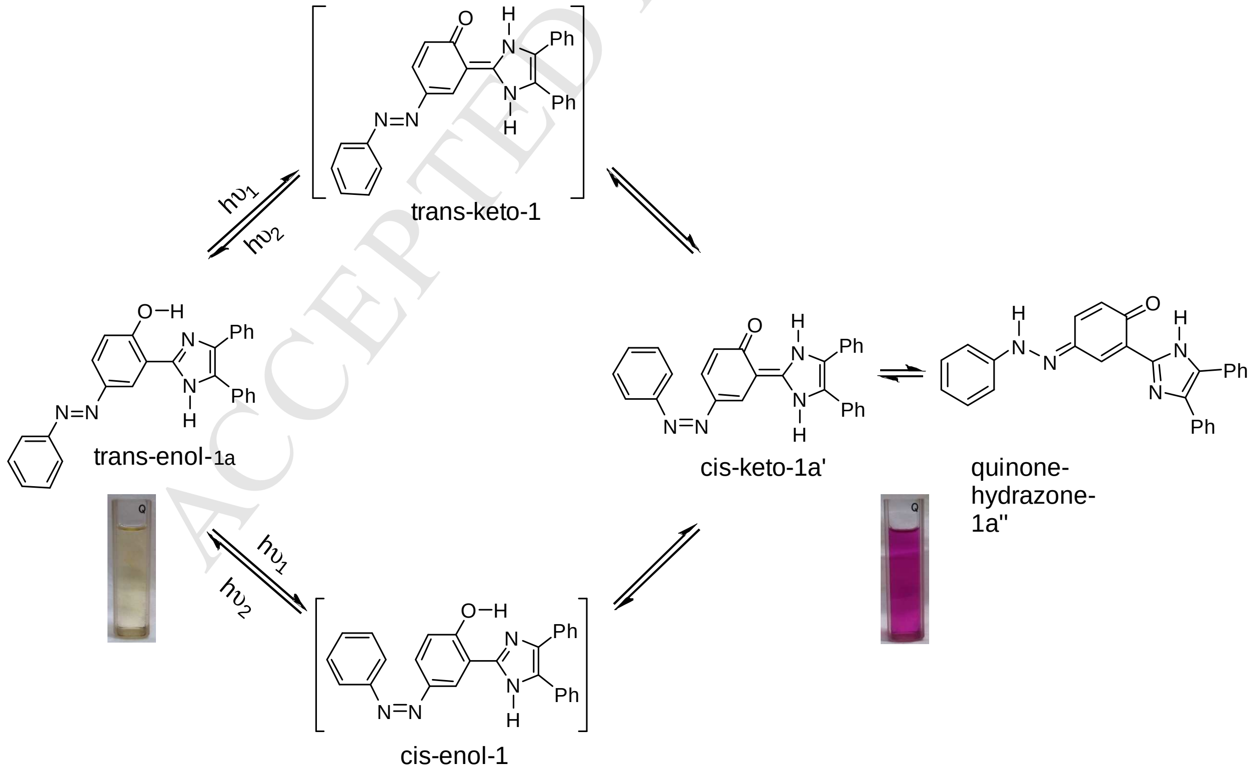
Product	Color	Time (min)	Recrystallization	mp (°C)	Yield%
1a	orange	2	EtOH	191-192	87
1b	orange	2.5	EtOH/$CHCl_3$	198-200	88
1c	dark orange	2	EtOH	215-217	82
1d	golden	2.5	EtOH	232-234	88
1e	golden	1.5	EtOH/$CHCl_3$	248-250	96
1f	orange red	2	EtOH/$CHCl_3$	277-278	95
1g	dark red	2	EtOH	250-251	96
1h	golden	1.5	EtOH/$CHCl_3$	230-232	92

Primarily AcOH glacial activated the carbonyl groups of either benzil or aldehyde to facilitate a nucleophilic attack of the nitrogen of NH_3 on the activated carbonyl group **2a** to produce intermediate **5**. Intermediate **5** in condensation with benzyl forms intermediate **6**, which in turn rearrange to the azo-imidazole **1a** via [1,5]-H shift (Scheme 2).



Scheme 2. Proposed mechanism for the synthesis of azo-imidazoles **1a-1h**

Photoisomerization of the azo-imidazoles **1a**-**1h** in $CHCl_3$ upon irradiation with 254 nm UV light were studied. All the compounds exhibit good photochromic behavior upon irradiation with alternative UV and visible light (See supporting data). The UV-Vis spectra of **1a** varying with the irradiation time and given in Fig. 1. Before UV irradiation the weak band at 244 nm and the strong band at 324 nm were observed. After UV-light irradiation, the absorption intensity at 324 nm gradually was decreased and a new absorption band at 537 nm was appeared. Prior to UV irradiation, *trans*-enol-**1a** photoisomer dominates in the solution and strong absorption band centered at 324 nm was observed. Under UV irradiation, an intramolecular proton transfer is induced and convert a pale yellow *trans*-enol-**1a** photoisomer to purple *cis*-keto-**1a´** and/or quinone-hydrazone-**1a˝** photoisomers via trans-keto-1, cis-enol-1 or both photoisomers. Beyond any reasonable doubt, the obtained isosbestic point reveals the equilibrium establishment of **1a** between *trans*-enol-**1a** and quinone-hydrazone-**1a˝** photoisomers (Scheme 3).



Scheme 3. Photochromic reaction **1a** in $CHCl_3$ solution

All compounds were shown very high thermal back relaxation and the purple or blue color of compounds by overnight staying in dark at room temperature returns back to initial color (cis→trans). Repeated irradiation showed little sign of degradation at least up to 20 cycles.

The UV–Vis absorbance spectra of **1g** with para nitro substitution in $CHCl_3$, before light irradiation, the weak band at 244 nm and broad absorption bands at 302, 405 (due to NO_2 group) were observed. This photoisomer under UV irradiation, the absorption intensity at 302 and 405 nm gradually decreased and a new absorption band at 537 nm was appeared, the color was changed from yellow to purple solution (Fig. 1, right).

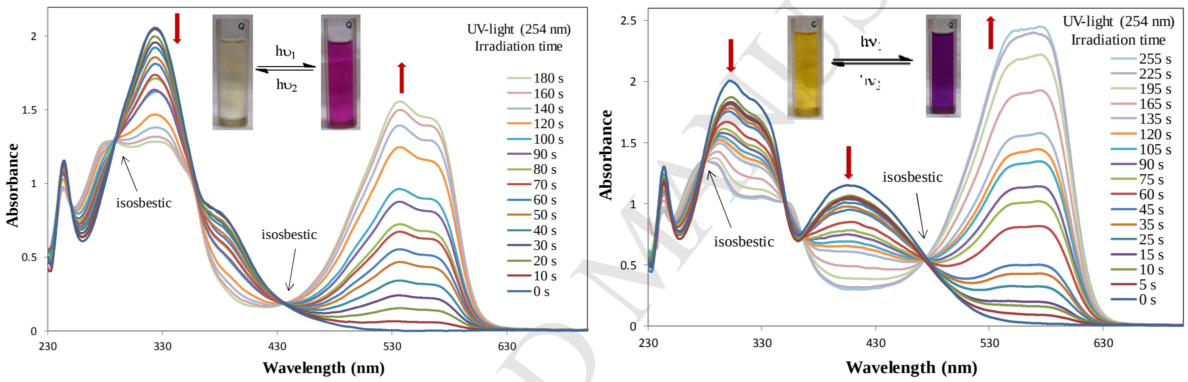


Fig. 1 The UV-Vis spectra of **1a** (left), **1g** (right) before and after UV light irradiation for various times in $CHCl_3$ ($c = 2.0 \times 10^{-4}$ M, 293 K).

4. Conclusions

Here, we incorporate an imidazole unit into an azo dye via three-component reaction between azo dye, benzil and NH_4OAc under microwave irradiation to obtained azo-imidazoles **1a-1h**. Short reaction time, simple workup procedure and use of inexpensive condition and solvent are advantages of the proposed procedure. All the azo-imidazoles exhibit excellent positive photochromic behavior upon irradiation under UV light irradiation.

Acknowledgments

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Highlight

One-pot three-component synthesis of new photochromic azo-imidazoles

Properties and photochromic structural behavior relationship (PSBR)

Excellent positive photochromic behavior

azo-imidazoles synthesis under microwave irradiation