EFFICIENT GREEN APPROACH FOR THE SYNTHESIS OF SPIRO[[INDOLINE-3,4′-PYRAZOLO[3,4-b]QUINOLINE] DIONES USING [NMP]H₂PO₄ AND SOLVATOCHROMIC AND pH STUDIES

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GRAPHICAL ABSTRACT

Abstract A mild and efficient protocol for the synthesis of spiro[indoline-3,4′-pyrazolo[3,4-b]quinoline]diones via a one-pot, three-component condensation of isatins, 1,3-dicarbonyls, and 5-amino-1-phenyl-3-methylpyrazole using [NMP]H₂PO₄ as a catalyst in EtOH/H₂O is described. The catalyst could be recycled and reused four times without significant loss of activity. Spiro[indoline-3,4′-pyrazolo[3,4-b]quinoline]diones with stabilized zwitter ionic resonance structures showed feasible application as new fluorescent probes and pH indicators. These chemosensors have a good wavelength shift and showed excellent sensitivity in the range of pH from 11 to 13.

Keywords 5-Amino pyrazole; β-diketones; ionic liquid; isatin; multicomponent reaction; spirooxindoles

INTRODUCTION

Multicomponent reactions (MCRs) provide unmatched opportunities for the enhancement of complexity and diversity in synthetic outcomes[1] by the facile
formation of several new covalent bonds in a one-pot transformation.[2] Synthesis of quinolines and indoles via MCRs has paved the way for diverse classes of heterocycles.[3] Significantly, 3-spiroheterocyclic 2-oxindole cores have been found in a number of natural products, such as alstonisine,[4] tabernoxidine,[5] and medicinally important NITD 609.[6] 3-Spiroheterocyclic 2-oxindoles show significant biological activities[7] and have emerged as potential fluorescent materials.[8] Isatin is a privileged lead molecule for designing potential bioactive agents, and its derivatives have been shown to possess a broad spectrum of bioactivities, such as anti-HIV,[9] antiviral,[10] antitumor,[11] antifungal,[12] and anticonvulsant[13] activities. Oxindoles have also been shown to possess mechanism-specific antiproliferative, antibacterial, antiprotozoal, and anti-inflammatory activities.[14–17]

The combination of green chemistry and MCRs offers very efficient protocols for the synthesis of complex heterocycles from both economic and environmental perspectives. The ionic liquids (ILs) have emerged as green solvents for synthesis and catalysis.[18–21] There are only a few reports about the synthesis of spirooxindole derivatives[22–25] in ionic liquid medium. We have been working on the applications of task-specific ionic liquid [NMP]H2PO4 as this can be prepared in one step without the use of organic solvents. We have attempted synthesis of spiro-oxindole derivatives.

RESULTS AND DISCUSSION

Chemistry

In this article, we report synthesis of tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-b]quinoline]-2,5'(1'H)-diones (4a–4k) by one-pot, three-component condensation of isatin (1), 5-amino-3-methyl-1-phenylpyrazole (2), and 1,3-dicarbonyl compounds (3) with [NMP]H2PO4 as a catalyst in EtOH:H2O (1:4) at 80 °C. The recyclability of catalyst has also been investigated. We have studied their photophysical properties also. These 3-spiroheterocyclic 2-oxindoles show intramolecular charge transfer and are potential fluorescent materials. The effect of pH on absorbance and fluorescence of all synthesized compounds has also been examined. The reaction conditions for the target reaction were optimized by attempting the reactions of isatin (1) (1.0 mmol), 5-amino-3-methyl-1-phenylpyrazole (2) (1.0 mmol), and dimesone (3a) (1.0 mmol). The reaction was first attempted in ethanol (5 mL) using para-toluenesulfonic acid (pTSA) (20 mol%) as catalyst. The reaction was incomplete even after 3 h as indicated by thin-layer chromatography (TLC; ethyl acetate/petroleum ether, 40:60, v/v) but resulted in the formation of a new product, which was identified as 3',7',7'-trimethyl-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-b]quinoline]-2,5'(1'H)-dione (30%) (4a) after separation (Table 1, entry 1). The reactions were then explored using 20 mol% of AcOH, [NMP]HSO4, and [NMP]H2PO4 as catalysts under otherwise identical conditions (Table 1, entries 2–4). The reactions resulted in the formation of 4a in 50, 65, and 75% yields, respectively. The reaction using [NMP]H2PO4 as catalyst that gave the greatest yield was then explored in different solvents and at different temperatures (Table 1, entries 5–11). It was observed that the reaction performed using [NMP]H2PO4 (20 mol%) as catalyst in H2O:EtOH (4:1, v/v) at 80 °C resulted in 92%
of 4a in 25 min (Table 1, entry 9). The same reaction attempted at greater temperature (100 °C) had no effect, whereas reaction at lower temperature (60 °C) gave inferior yields (entries 10–11). The reaction using 10 mol% of catalyst gave inferior yield (entry 12), and using 30 mol% of catalyst did not affect the yield (entry 13) (Scheme 1).

Encouraged by these results, we investigated the scope of the reaction of 5-amino-1-phenyl-3-methylpyrazole (2) with different isatins (1) and 1-3-dicarbonyls (3) under optimized reaction conditions (Scheme 2). All the reactions were complete in 15–30 min and gave the corresponding products in good yields by a simple workup.

All the products were characterized using 1H NMR, 13C NMR, infrared (IR), and meltin point (mp). A proposed mechanism for the synthesis of 4 using [NMP]H2PO4 is depicted in Scheme 3.

The possibility of recycling the catalyst [NMP]H2PO4 was also examined using the reaction of isatin (1), 5-amino-3-methyl-1-phenyl-pyrazole (2), and dimedone (3a) under optimized conditions. Upon completion of the reaction, the product was filtered at the suction pump and washed with water. To recover the catalyst, H2O and ethanol were removed under reduced pressure, and the resulting liquid was washed with diethyl ether and dried to recover [NMP]H2PO4. The recovered

![Scheme 1](image1.png)

**Scheme 1.** Synthesis of 3',7',7'-trimethyl-1'-phenyl-6',7',8',9'-tetrahydropirano[indoline-3,4'-pyrazolo[3,4-b]quinoline]-2,5'(1'H)-dione (4a).
catalyst could be reused four times after which there was a significant decrease in the activity of the catalyst (Fig. 1).

Photophysical Studies

The design and synthesis of new fluorescent probes has attracted considerable attention for a variety of applications\cite{29-31} such as telecommunications, optical

Scheme 2. Synthesis of spiro[indoline-3,4′-pyrazolo[3,4-\textit{b}]quinoline]-2,5′(1′\textit{H})-dione (4a–4k).

Scheme 3. Proposed mechanism for the synthesis of spirooxindole derivatives 4.
computing, optical storage, fluorescent probes, and fluorescent chemosensors for biologically important metal ions. Therefore, we explored the photophysical properties of all synthesized compounds.

Absorption and Emission Characteristics

The spectral properties of all the compounds (4a–4k) were measured in methanol. The $1.0 \times 10^{-6}$ mol L$^{-1}$ solution of all compounds showed single absorption band in the region of 319–358 nm (Fig. 2). Moreover, when these compounds were excited at 320 nm, they exhibited strong photoluminescent emissions with the emission maxima ranging from 412 to 437 nm (Fig. 3). The spectrophotometric properties of the compounds such as absorption maxima ($\lambda_{\text{max}}$), emission maxima ($\lambda_{\text{em}}$), and Stokes shift ($\Delta \nu$) are reported in Table 3. The large magnitude of Stokes shift was observed for all the compounds (4a–4k), which indicates that the excited state geometry could be different from that of the ground state.

![Graph showing recyclability of the catalyst.](image)

**Figure 1.** Recyclability of the catalyst.

![Graph showing absorption spectra.](image)

**Figure 2.** Absorption spectra of 4a–4k in methanol ($1 \times 10^{-6}$ M).
Effects of Solvent Polarity on Absorption and Emission Spectra

The effect of solvent polarities on photophysical properties of 4d was investigated in nine solvents of varying polarity. Effects of solvent polarity on absorption and emission spectra of this compound are shown in Figs. 4 and 5, respectively and are summarized in Table 4. It is clear from Table 4 that compound 4d showed

Table 2. Synthesis of spiro[indoline-3,4'-pyrazolo[3,4-b]quinoline]-2,5'-dione (4a-4k)\(^a\)

| Product | R   | 1,3-Dicarbonyl | Time (min) | Yield (%) | M.p. (°C) Obs. | M.p. (°C) Lit. |
|---------|-----|----------------|------------|-----------|----------------|----------------|
| 4a      | H   | 3a             | 25         | 92        | 242-244        | 241-243\(^{[26]}\) |
| 4b      | H   | 3b             | 15         | 88        | >300           | >300\(^{[27]}\)  |
| 4c      | H   | 3c             | 20         | 89        | >300           | 315-318\(^{[26]}\) |
| 4d      | H   | 3d             | 20         | 87        | >300           | 335-337\(^{[26]}\) |
| 4e      | H   | 3e             | 30         | 88        | 300\(^b\)     |                |
| 4f      | Br  | 3a             | 25         | 90        | 301-303        |                |
| 4g      | Br  | 3c             | 30         | 90        | 359-361\(^b\) | >300\(^{[28]}\) |
| 4h      | NO2 | 3a             | 15         | 90        | 288-290\(^b\) | >300\(^{[29]}\) |
| 4i      | NO2 | 3b             | 20         | 87        | 327-329\(^b\) |                |
| 4j      | NO2 | 3c             | 20         | 89        | 305-307\(^b\) |                |
| 4k      | NO2 | 3d             | 20         | 92        | 339-341\(^b\) |                |

\(^a\)Reaction of isatin (1), 5-amino-3-methyl-1-phenylpyrazole (2), and 1,3-dicarbonyl compounds (3) in the presence of [NMP]H2PO4 in H2O:EtOH (4:1) at 80 °C.

\(^b\)Decomposition.

Table 3. Photophysical data of compounds 4a-4k in methanol (1.0 × 10^{-6} M)

| Product | \(\lambda_{\text{max}}\) (nm) | \(\lambda_{\text{em}}\) (nm) | Stokes shift (\(\Delta\nu\)) (cm\(^{-1}\)) |
|---------|-----------------------------|-----------------------------|----------------------------------|
| 4a      | 338                         | 430                         | 6330                            |
| 4b      | 337                         | 428                         | 6309                            |
| 4c      | 336                         | 430                         | 6506                            |
| 4d      | 320                         | 413                         | 7037                            |
| 4e      | 352                         | 418                         | 4486                            |
| 4f      | 332                         | 430                         | 6864                            |
| 4g      | 339                         | 428                         | 6134                            |
| 4h      | 358                         | 413                         | 3720                            |
| 4i      | 332                         | 413                         | 7237                            |
| 4j      | 334                         | 413                         | 5786                            |
| 4k      | 319                         | 413                         | 7076                            |
bathochromic shift in absorption and emission maxima in polar solvents such as water and methanol relative to nonpolar solvents like benzene and hexane. There is a significant increase in Stokes shift with increasing polarity from hexane and benzene to water and methanol for compound 4d. This significant increase in Stokes shift indicates a larger charge transfer taking place in the excited state in comparison to the ground state. The Stokes shift of compound 4d in different solvents has been correlated with solvent polarity parameter $\Delta f$ (orientation polarizability) to study the specific solvent-fluorophore interactions (Fig. 6). The Lippert–Mataga plot of the Stokes shift ($\Delta v$) as a function of solvent polarity parameter $\Delta f$ does not follow the classical behavior when both polar and nonpolar solvents are employed, which suggests that specific solute–solvent interactions are not negligible. The deviation of Stokes shift from linearity in water and methanol could be due to the hydrogen bonding with donor atoms.

Figure 4. Absorption spectra of 4d ($1.0 \times 10^{-6} \text{ M}$) in different solvents.

Figure 5. Fluorescence spectra of 4d ($1.0 \times 10^{-6} \text{ M}$) in different solvents.
Effects of Different pH Values on Absorption and Emission Spectra

The effects of different pH values on absorption and emission spectra of compound 4d were also investigated by adding different amounts of HCl and KOH to the solutions of compound 4d (1.0 × 10⁻⁶ M in methanol). The absorption spectra of compound 4d is not sensitive to the addition of acid, but the absorption spectra is sensitive to the addition of base, although not at all the examined pH values. The absorption band did not show any shift at low basic pH values (7.6, 8.3, 9.6, 10.2) but it showed a large bathochromic shift of 48 nm from $\lambda_{\text{max}}$ of 314 nm to $\lambda_{\text{max}}$ of 362 nm at high basic pH values (>10.2) (Fig. 7). These results suggest that tautomeric form of compound 4d in methanol changes to another tautomeric form on addition of base.

The effects of acid and base on emission spectra of compound 4d in methanol (1.0 × 10⁻⁶ M) was also investigated (Fig. 8). Emission spectra of compound 4d showed a slight bathochromic shift of 7 nm at high acidic pH value and no effect was observed at less acidic pH values. Also a bathochromic shift of 21 nm from

| S. no. | Solvent      | $\lambda_{\text{max}}$ (nm) | $\lambda_{\text{em}}$ (nm) | Stokes shift (cm⁻¹) | Orientation polarizability ($\Delta\beta$) |
|--------|--------------|-----------------------------|---------------------------|---------------------|------------------------------------------|
| 1.     | Methanol     | 319.3                       | 422                       | 7602                | 0.3090                                   |
| 2.     | Acetonitrile | 314                         | 396                       | 6594                | 0.3046                                   |
| 3.     | Benzene      | 309                         | 372                       | 5480                | 0.003                                    |
| 4.     | Chloroform   | 318                         | 394                       | 6066                | 0.148                                    |
| 5.     | Dichloromethane | 317.5             | 398                       | 6370                | 0.217                                    |
| 6.     | DMF          | 316.5                       | 398                       | 6469                | 0.274                                    |
| 7.     | Ethyl acetate| 314                         | 388                       | 6074                | 0.199                                    |
| 8.     | Hexane       | 308                         | 370                       | 5440                | 0.001                                    |
| 9.     | Water        | 319                         | 424                       | 7763                | 0.3199                                   |

Figure 6. Lippert–Mataga plot for compound 4d.
416 to 437 nm was observed in emission spectra of compound 4d at high basic pH values. This shift could be due to change in the tautomeric form of 4d.

CONCLUSION

We have developed a simple, one-pot, three-component procedure for the preparation of biologically interesting oxindole derivatives using ionic liquid [NMP]H₂PO₄ in H₂O/EtOH (4:1 v/v) as reaction medium. Effects of solvent polarity on absorption and emission spectra of compound 4d showed that absorbance and fluorescence spectra depend on solvent polarity and showed good correlation to Lippert–Mataga plot. It has been observed that absorption and emission spectra show high bathochromic shift at pH range of 11.4–13.2.
EXPERIMENTAL

Structures of all of the compounds were identified by their spectroscopic data. Silica gel 60 F254 (precoated aluminum plates) from Merck were used to monitor the reaction progress. Melting points were determined on a Tropical labequip apparatus and are uncorrected. IR (KBr) spectra were recorded on a Perkin–Elmer FTIR spectrophotometer and the values are expressed as \( \nu_{\text{max}} \) in cm\(^{-1}\). The NMR (\(^1\)H and \(^{13}\)C) spectra were recorded on a Jeol JNM ECX-400P at 400 and 100 MHz, respectively. The chemical shift values are recorded on the \( \delta \) scale and the coupling constants (\( J \)) are in hertz. Mass spectra were recorded on a Waters Alliance 2695 high-performance liquid chromatograph (HPLC) with Quatromicro-Triple Quadrupole MS.

General Procedure for the Synthesis of Compounds 4a–4k

A mixture of isatin (1) (1.0 mmol), 5-amino-3-methyl-1-phenylpyrazole (2) (1.0 mmol), 1,3-dicarbonyl compounds (3) (1.0 mmol), and [NMP]H2PO4 (20 mol\% in H\(_2\)O = EtOH (4:1 v/v)) was placed in a 100-ml round-bottomed flask, which was stirred at 80 °C on a preheated oil bath for an appropriate time as shown in Table 2. After completion of the reaction as confirmed by thin-layer chromatography (TLC; ethyl acetate = petroleum ether, 40:60 v/v), the reaction mixture was cooled to room temperature. The precipitated product was filtered at pump, washed with water = ethanol (1:1), and dried. It was recrystallized from ethanol to afford the pure products (4a–4k) in excellent yield. All the products were characterized using \(^1\)H NMR, \(^{13}\)C NMR, IR, and mass spectra.

Spectral Data

\( 3',6',8'-\text{Trimethyl-1'-phenylspiro[indoline-3,4'-pyrazolo[3,4-b]pyrido[2,3-d]-pyrimidine]-2,5',7'(1'H, 6'H, 8'H, 9'H)trione (4e). White, yield 88\%, mp 300 °C. IR (\( \nu_{\text{max}}, \) cm\(^{-1}\)) (KBr): 3214, 1708, 1615, 1550, 1209, 1117, 757, 680; \(^1\)H NMR (400 MHz, DMSO d\(_6\)): \( \delta \): 9.53 (s, 1H, N-H), 7.68 – 7.66 (m, 2H, Ar-H), 7.55 – 7.51 (m, 2H, Ar-H), 7.37 – 7.34 (m, 1H, Ar-H), 7.15 – 7.12 (m, 1H, Ar-H), 6.89 – 6.83 (m, 3H, Ar-H), (NMe) 1.57 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, DMSO d\(_6\)): \( \delta \): 178.6, 159.9, 150.5, 144.6, 142.0, 138.4, 135.6, 129.4, 127.7, 126.6, 123.3, 121.7, 121.6, 108.8, 101.7, 48.5, 48.4, 30.5, 30.0, 28.9, 27.5, 17.1, 11.2. MS (ESI) \( m/z \) [M\(^+\) + H] calculated for C\(_{24}\)H\(_{21}\)N\(_6\)O\(_3\): 441.16; found: 441.25.

\( 3',6',8'-\text{Dimethyl-5-nitro-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-b]quinoline]-2,5'(1'H)-dione (4i). Yellow, yield 87\%, mp 327–329 °C. IR (\( \nu_{\text{max}}, \) cm\(^{-1}\)) (KBr): 3229, 3149, 2946, 1726, 1612, 1533, 1472, 1335, 1127, 754, 690; \(^1\)H NMR (400 MHz, DMSO d\(_6\)): \( \delta \): 9.94 (s, 1H, N-H), 8.13 – 8.10 (m, 1H, Ar-H), 7.74 – 7.70 (m, 1H, Ar-H), 7.54 – 7.40 (m, 5H, Ar-H), 7.03 – 7.01 (m, 1H, Ar-H), 2.80 – 2.34 (m, 2H, CH\(_2\)), 2.23 – 2.07 (m, 2H, CH\(_2\)), 2.01 – 1.94 (m, 1H, Ar-H), 2.80 – 2.34 (m, 2H, CH\(_2\)), 0.99 – 0.98 (m, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, DMSO d\(_6\)): \( \delta \): 193.7, 180.2, 148.3, 144.6, 142.2, 137.8, 137.6, 129.4, 127.5, 125.1, 123.8, 118.7, 118.5, 108.7, 107.9, 107.6, 100.2, 100.1, 48.8, 44.6, 35.2, 28.3, 28.1, 20.3, 11.4; MS (ESI) \( m/z \) [M\(^+\)+H] calculated for C\(_{25}\)H\(_{22}\)N\(_5\)O\(_4\): 456.16; found: 456.31.
3'-Methyl-5-nitro-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-b]quinoline]-2,5(1'H)-dione (4j). Yellow, yield 89%, mp 305–307 °C. IR (υmax, cm⁻¹) (KBr): 3147, 3048, 2928, 1727, 1611, 1525, 1472, 1333, 1124, 752, 691; ¹H NMR (400 MHz, DMSO d6): δ: 9.93 (s, 1H, N-H), 8.10–8.07 (m, 1H, Ar-H), 7.71–7.70 (m, 1H, Ar-H), 7.53–7.48 (m, 4H, Ar-H), 7.41–7.36 (m, 1H, Ar-H), 7.0–6.98 (m, 1H, Ar-H), 2.75–2.59 (m, 2H, CH₂), 2.20–2.04 (m, 2H, CH₂), 1.94–1.80 (m, 2H, CH₂), 1.53 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO d6): δ: 193.9, 180.2, 156.0, 148.3, 144.6, 142.2, 137.8, 137.6, 136.8, 129.4, 127.5, 125.1, 123.8, 118.6, 108.7, 108.2, 100.1, 48.9, 36.7, 27.6, 20.9, 11.4. MS (ESI) m/z [M+2H] calculated for C₂₄H₂₀N₅O₄: 442.15; found: 442.24.

3-Methyl-5'-nitro-1-phenyl-6,7-dihydro-1H-spirocyclopenta[e]pyrazolo[3,4-b]pyridine-4,3'-indoline]-2,5(8H)-dione (4k). Yellow, yield 92%, mp 339–341 °C. IR (υmax, cm⁻¹) (KBr): 3197, 3150, 2928, 1727, 1616, 1539, 1474, 1333, 1108, 759, 697; ¹H NMR (400 MHz, DMSO d6): δ: 10.7 (s, 1H, N-H), 8.18–8.16 (m, 1H, Ar-H), 7.816–7.810 (m, 1H, Ar-H), 7.57–7.56 (m, 4H, Ar-H), 7.47–7.42 (m, 1H, Ar-H), 7.09–7.07 (m, 1H, Ar-H), 2.82–2.70 (m, 2H, CH₂), 2.30–2.27 (m, 2H, CH₂), 1.55 (m, 3H, CH₃) ¹³C NMR (100 MHz, DMSO d6): δ: 199.5, 178.8, 167.9, 148.1, 145.1, 142.5, 139.8, 139.5, 129.5, 127.6, 125.5, 123.7, 119.7, 112.0, 109.2, 100.3, 47.2, 33.3, 30.6, 24.7, 11.3. MS (ESI) m/z [M+H] calculated for C₂₃H₁₈N₅O₄: 428.13; found: 428.22.

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SUPPORTING INFORMATION
Supplemental data for this article can be accessed on the publisher’s website.

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