

Synthesis of Some Novel 3-[(2-Hydrazono) Benzimidazolyl]-2-Indolinone as Possible Azodyes

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Indole-2,3-diones have been condensed with 2-hydrazinobenzimidazole to yield 3-[(2-hydrazono)benzimidazolyl]-2-indolinone (III). Structural investigation showed that the title compound exists in two tautomeric forms (III–III'), both being stabilized by hydrogen-bonding. The dark yellow colour and the structure indicates the possible use of these compounds as azodyes. Further, N-substituted derivatives have been synthesized by three different methods: (i) starting with N-substituted indole-2,3-dione, (ii) starting with N-substituted 2-hydrazinobenzimidazole, (iii) by carrying out the substitution on nitrogen after preparation of the title compound. The synthesized compounds have been characterised by elemental analysis, IR, ¹H-NMR and mass spectral studies.

INTRODUCTION

Indole-2,3-dione¹ and 2-hydrazinobenzimidazole² are very reactive compounds. Although the reactions of indole-2,3-dione with phenyl-hydrazines have been studied earlier^{3,4}, but the reaction with 2-hydrazinobenzimidazole has been investigated for the first time by us during our comprehensive programme to synthesise novel indole derivatives.

In view of this we have synthesized several 3-[(2-hydrazono-benzimidazolyl)]-2-indolinones (III). Simple and N-substituted indole-2,3-diones were reacted with simple and N-substituted 2-hydrazinobenzimidazole in the presence of glacial acetic acid in ethanol, resulting in the formation of (III). These compounds exist in two tautomeric forms (III–III') and both the forms are stabilised by H-bonding. The dark yellow colour and structure indicates possible use of these compounds as azodyes. (Scheme-1)

RESULT AND DISCUSSION

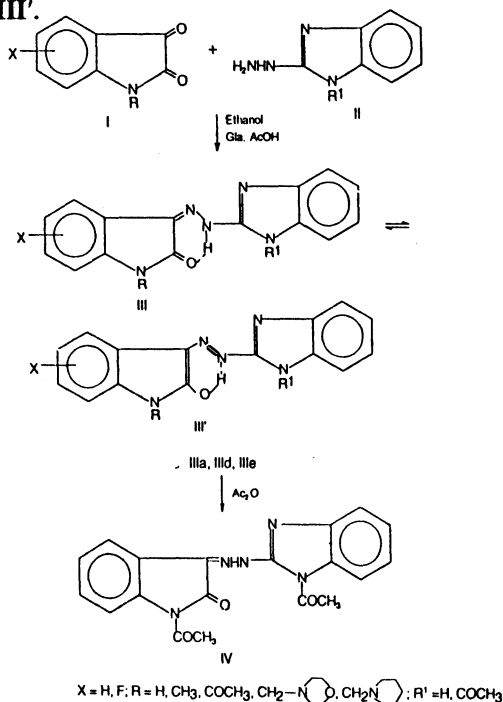
Formation of III was confirmed by the absorption bands at 1690–1710 (C=O), 1590–1610 (C=N) and 3000–3100 (NH/OH) in the IR spectra and singlets at δ 8.5, 9.5 and 10.5 ppm (NH and =NNH/OH) was observed in the ¹H NMR spectra. Further, structure was confirmed by mass spectra *e.g.* IIIa shows M⁺ at m/e 227.

Compound III can exist in the tautomeric forms III and III', both the forms are stabilized by H-bonding. The hydrogen bonding was confirmed by the IR

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spectra, the broad band in the region $3000\text{--}3100\text{ cm}^{-1}$ is assigned to --OH of the enolic form of the molecule⁴.

Acetylation of **IIIa** ($\text{R}=\text{R}'=\text{H}$), **IIIId** ($\text{R}=\text{COCH}_3$, $\text{R}'=\text{H}$) as well as **IIIe** ($\text{R}=\text{H}$, $\text{R}'=\text{COCH}_3$) afforded the same product, which was confirmed as the diacetylated derivative instead of triacetylated derivative. In the IR spectrum it shows absorption bands at $1680\text{--}1700$ ($\text{C}=\text{O}$) and $3000\text{--}3100$ ($=\text{NNH}/\text{OH}$) cm^{-1} and in the $^1\text{H-NMR}$ spectrum singlets appear at δ 2.1 and 2.5 (both COCH_3) and 10.2 ($=\text{NNH}/\text{OH}$) ppm. In the mass spectrum M^+ appears at m/e 361. Since, no acetylation took place at $=\text{NNH}$, it further confirms the existence of **III** in the tautomeric form **III'**.



SCHEME 1

EXPERIMENTAL

Purity of all the compounds was checked on silica gel G plates using iodine vapour as the detecting agent. Melting points were determined in open capillary tubes using Gallenkamp melting point apparatus and are uncorrected. IR spectra ($\nu_{\text{max}}\text{ cm}^{-1}$) were recorded on a Perkin Elmer 577 spectrophotometer in KBr pellets. $^1\text{H-NMR}$ spectra (DMSO-d_6) were recorded at 89.99 MHz using JEOL (model FX-90Q) machine and TMS is used as internal standard. The mass spectra were recorded on Kratos MS-30 and MS-50 spectrometer operating at an ionization potential of 70 eV. The elemental analyses were performed at Central Drug Research Institute (CDRI) Lucknow, India, and are uncorrected.

Indole-2, 3-diones (I)^{5, 6} (isatins) and **2-hydrazinobenzimidazoles**⁷ (II)

These compounds have been synthesized by the literature methods.

TABLE I
CHARACTERIZATION DATA OF COMPOUNDS III

Compound	X	R	R ¹	Yield %	M.pt. °C	Molecular formula	Analysis					
							Found (%)			Calculated (%)		
							C	H	N	C	H	N
IIIa	H	H	H	89	320	C ₁₅ H ₁₁ N ₅ O	65.01	4.01	25.30	64.98	3.97	25.27
IIIb	F	H	H	88	315	C ₁₅ H ₁₀ FN ₅ O	61.09	3.42	23.81	61.01	3.38	23.73
IIIc	H	CH ₃	H	85	311	C ₁₆ H ₁₃ N ₅ O	66.01	4.49	24.08	65.97	4.46	24.05
IIId	H	COCH ₃	H	87	290	C ₁₇ H ₁₃ N ₅ O ₂	63.99	4.10	21.10	63.94	4.07	21.94
IIIe	H	H	COCH ₃	84	281	C ₁₇ H ₁₃ N ₅ O ₂	63.98	4.11	21.99	63.94	4.07	21.94
IIIf	H	MM*	H	80	288	C ₂₀ H ₂₀ N ₆ O ₂	63.88	5.35	22.40	63.82	5.31	22.34
IIIg	H	PM†	H	82	310	C ₂₁ H ₂₂ N ₆ O	67.40	5.91	22.41	67.37	5.88	22.45

*MM = Morpholinomethyl

†PM = Piperidinomethyl

3-[(2-hydrazono) benzimidazolyl] indolinone (IIIa)

Indole-2,3-dione (1.47 g; 0.01 mole), 2-hydrazinobenzimidazole (1.48 g; 0.01 mole), ethanol (50 mL) and 3–4 drops of gla. acetic acid refluxed for 5 hrs. After cooling at room temperature, solid obtained was filtered, washed with ethanol and finally recrystallised from ethanol.

Yield: 2.4 g, 89%, m.pt.; 320°C; IR spectrum (KBr, cm^{-1}): 1610vs $\nu(\text{C}=\text{N}/\text{N}=\text{N})$, 1700s $\nu(\text{C}=\text{O})$ and 3000–3100br $\nu(\text{NH}/\text{OH})$; $^1\text{H-NMR}$ spectrum (DMSO-d_6 ; δ ppm): 6.8–7.8 (m, 8H, Ar-H); 8.5 (s, 1H, MH benz.), 9.5 (s, 1H, NH isatin) and 10.5 (s, 1H, =NNH/OH); mass spectrum (MS): m/e 277 (M^+), 278 ($\text{M} + 1$).

Elemental analyses: Found: C, 65.01; H, 4.01; N, 25.30. $\text{C}_{15}\text{H}_{11}\text{N}_5\text{O}$ require C, 64.98; H, 3.97; N, 25.27%.

All other compounds (III b–g) were prepared in a similar manner (Table 1)

1-Acetyl-3-[1-acetyl-2-hydrazono) benzimidazolyl]-2-indolinone (IV)

It was prepared in three ways:

1. IIIa (2.77 g; 0.01 mole) was refluxed with acetic anhydride (30 mL) for 6 hrs. The product so obtained was cooled, filtered and washed with solvent ether to give IV.

2. III d (3.19 g; 0.01 mole) was refluxed with acetic anhydride (30 mL) for 6 hrs and treated in a similar manner as in 1, to give IV.

3. It was similarly prepared from III e (3.19 g; 0.01 mole) and acetic anhydride.

IV, prepared by three different ways, has the same m.pt., analytical and spectral data. M.pt.: 275°C; Yield: 81–90%; IR spectrum (KBr; cm^{-1}): 1620s $\nu(\text{C}=\text{N}/\text{N}=\text{N})$, 1660, 1700s $\nu(\text{C}=\text{O})$ and 3000–3090br $\nu(\text{NH}/\text{OH})$; $^1\text{H-NMR}$ spectrum (DMSO-d_6 ; δ ppm): 2.1 and 2.5 (both s, 3H, COCH_3), 6.7–7.6 (m, 8H, Ar-H) and 10.2 (s, 1H, =NNH/OH); mass spectrum (MS): m/e 361 (M^+).

Elemental analyses: Found: C, 63.19; H, 4.18; N, 19.32; $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}_3$ requires C, 63.15; H, 4.15; N, 19.39%.

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