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Maruti Aldar
The Institute of Science, Dr. Homi Bhabha University, Mumbai, Maharashtra, India

Shardini Wakchoure
The Institute of Science, Dr. Homi Bhabha University, Mumbai, Maharashtra, India

Vinayak Patil
The Institute of Science, Dr. Homi Bhabha University, Mumbai, Maharashtra, India

Vishal Banewar
The Institute of Science, Dr. Homi Bhabha University, Mumbai, Maharashtra, India

Correspondence
Vishal Banewar
The Institute of Science, Dr. Homi Bhabha University, Mumbai, Maharashtra, India

Design, synthesis, and spectroscopic characterization of electron-withdrawing substituted formazans

Maruti Aldar, Shardini Wakchoure, Vinayak Patil and Vishal Banewar

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Abstract
An efficient synthetic route has been developed for the preparation of formazan derivatives bearing electron-withdrawing groups. This methodology facilitated the synthesis of compounds substituted with cyano and nitro moieties at the 3-position, isolated in high purity and appreciable yields. The structures of these compounds were extensively characterized via infrared (IR), proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR), ultraviolet-visible (UV-Vis) spectroscopy, and mass spectrometry. Distinctive spectral markers, including the pronounced cyano stretching band near 2262 cm^{-1} and nitro group vibrations at approximately 1570 and 1353 cm^{-1}, confirmed the successful incorporation of these substituents. UV-Vis analysis revealed a significant bathochromic shift in the nitro derivative relative to the cyano analog, underscoring the profound impact of electron-withdrawing groups on the azo chromophore. This research highlights a viable synthetic strategy and provides insight into how electronic substituents influence the structural and spectroscopic properties of formazans.

Keywords: Formazans, azo compounds, electron-withdrawing groups, cyano substitution, nitro substitution, organic synthesis, spectroscopic characterization

1. Introduction
Formazans constitute a distinct category of nitrogen-containing heteroaromatic compounds characterized by their azo-imine (-N=N=C=N-) framework. Their multifaceted utility spans dye chemistry, sensor development, analytical reagents, pharmaceuticals, and coordination chemistry [1-5]. The structural flexibility and potent chromophoric properties of formazans make them a subject of sustained interest in both fundamental research and technological applications. Substitution of various groups onto the formazan core drastically alters the physicochemical characteristics. Electron-withdrawing substituents such as cyano (-CN) and nitro (-NO_2) significantly influence electron distribution, molecular stability, solubility, and optical behavior [9-13]. However, despite their relevance, systematic syntheses and comparative studies of these derivatives—particularly when substitution occurs at the electronically-sensitive 3-position—are scarce [14-17]. Therefore, this study aims to establish an efficient synthetic approach for 3-substituted formazans bearing electron-withdrawing groups and to analyze how these substituents affect molecular structure and spectroscopic properties through a combination of vibrational, nuclear magnetic resonance, UV-Vis, and mass spectrometric techniques [18-23].

2. Experimental Section
2.1 Materials and Methods
Reagents and solvents of analytical grade were employed as received, without further purification except where noted. Reaction progression was monitored via thin-layer chromatography (TLC). Melting points were determined using the capillary method.

2.2 Synthetic Procedure
Synthesis of 1,5-bis(4-bromophenyl)-3-cyanoformazan
In a chilled solution (-5 °C) containing 6.88 g (40 mmol) of 4-bromoaniline, 10 mL of 12 M hydrochloric acid, and 10 mL water, sodium nitrite (3.00 g, 43 mmol) was added slowly over 10 min with continuous stirring. After 15 minutes, this diazonium salt was introduced dropwise into an aqueous solution consisting of cyanoacetic acid (1.70 g, 20 mmol) and sodium hydroxide (8.00 g, 200 mmol) maintained at 0 to -5 °C over 30 minutes. The resultant mixture was filtered, and the organic layer extracted with dichloromethane (3 × 250

mL). Evaporation of the solvent yielded a dark orange solid, which was purified by column chromatography over neutral alumina using dichloromethane, producing a brick-red microcrystalline solid (3.96 g, 48.65% yield).

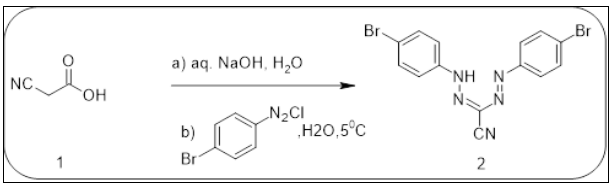


Fig 1: Reaction Pathway for Scheme 1

Synthesis of 1,5-bis(4-bromophenyl)-3-nitroformazan

In a similar manner, 15.82 g (92 mmol) of 4-bromoaniline was dissolved in 25 mL of 12 M hydrochloric acid and 50 mL water at 0 to 5 °C. Sodium nitrite (7.52 g, 109 mmol) was added incrementally over 10 minutes. After stirring for 30 minutes, the diazonium solution was added slowly to a cooled mixture of nitromethane (2.82 g, 46 mmol), sodium hydroxide (8.00 g, 100 mmol), and water (100 mL). The material formed was filtered, triturated with methanol, and purified via recrystallization from hot methanol, yielding a poppy red crystalline solid (9.82 g, 50.10% yield). Careful addition of the diazonium salt was crucial to prevent formation of an undesired brown oil, which complicated purification and reduced yield.

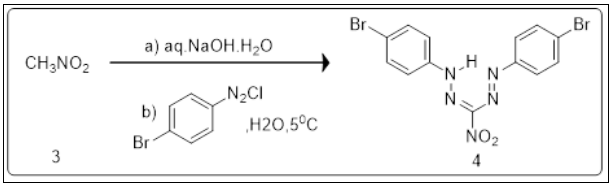


Fig 2: Reaction Pathway for Scheme 2

2.3 Characterization Techniques

Fourier-transform infrared (FTIR) spectra were recorded using KBr pellet preparation, scanning the 4000-400 cm^{-1} range. Proton and carbon-13 nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were acquired at 100 MHz using $CDCl_3$ as solvent. Ultraviolet-visible (UV-Vis) absorption spectra were collected in acetonitrile between 200 and 800 nm. Mass spectrometry verified molecular ion peaks consistent with the expected molecular masses.

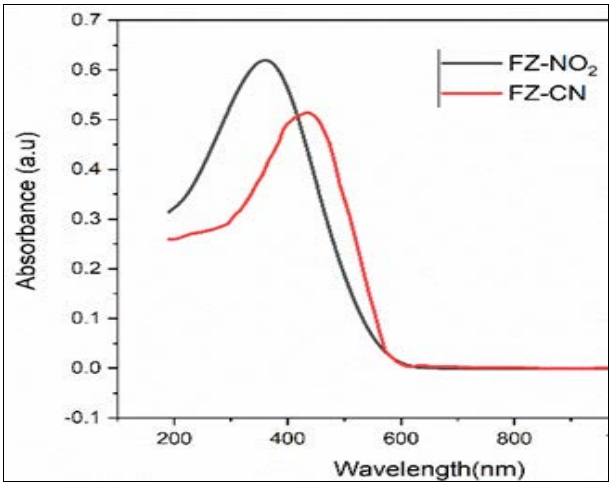
3. Results and Discussion

3.1 Synthesis

The electron-withdrawing cyano- and nitro-substituted formazans were synthesized reliably in yields of 48.65% and 50.10%, respectively. Both compounds crystallized as intensely colored solids — the cyano derivative as brick red and the nitro as poppy red, indicative of an extended conjugated azo-imine system.

3.2 Infrared Spectroscopy

The cyano-substituted formazan exhibited a strong absorption peak at 2262 cm^{-1}, consistent with the nitrile stretching vibration. For the nitro derivative, asymmetric and symmetric NO_2 stretching bands appeared at 1570.66 and 1353.14 cm^{-1}, respectively. Both compounds retained the characteristic azo (-N=N-) stretching vibrations observed between 1347 and 1660 cm^{-1}.



3.3 NMR Spectroscopy

^1H NMR spectra showed aromatic proton resonances between δ 7.20 and 8.5 ppm. The imine proton was identified as a singlet at δ 8.5-9.8 ppm. The cyano-substituted formazan exhibited downfield shifts for protons adjacent to the cyano group, while the nitro-substituted derivative demonstrated intensified deshielding effects across the aromatic region, consistent with the stronger electron-withdrawing nature of the nitro group. The ^{13}C NMR spectrum assisted in confirming structures with a diagnostic cyano carbon resonance near 116 ppm and nitro-substituted aromatic carbons resonating near 135.8 ppm.

3.4 UV-Visible Spectroscopy

Both derivatives displayed intense absorption bands from 350 to 500 nm pertinent to π-π* transitions within the extended azoimine conjugation. A bathochromic shift was evident in the spectrum of the nitro-substituted compound relative to its cyano counterpart, attributable to enhanced intramolecular charge transfer facilitated by the nitro substituent.

3.5 Mass Spectrometry

Mass spectral data exhibited molecular ion peaks consistent with theoretical molecular weights ($[M]^+$ at m/z 406 for the cyano-substituted compound), including isotopic distributions verifying bromine presence and confirming anticipated molecular structures.

4. Conclusion

A novel and efficient synthetic methodology was successfully demonstrated for the preparation of electron-withdrawing substituted formazans. The cyano- and nitro-substituted derivatives, obtained in good yields and purity, were fully characterized through complementary spectroscopic and analytical techniques. The data highlighted significant substituent effects on vibrational, electronic, and optical properties. The absorption maximum of the cyano-substituted formazan occurred near 437 nm whereas the nitro analog exhibited a hypsochromic shift to 361 nm. Nitro-substituted derivatives were more intensely colored but relatively less stable under ambient conditions compared to cyano-substituents. These findings accentuate the critical role of substituent electronic character in modulating the physical and spectral attributes of formazans, informing future molecular and materials design.

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