



SYNTHESIS AND SOLVATOCHROMIC PROPERTIES OF NOVEL AZO- AZOMETHINE DYES



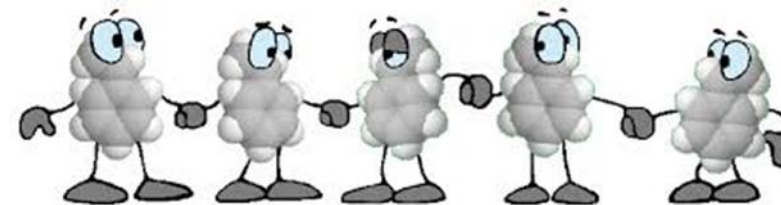
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Azomethines – Schiff bases

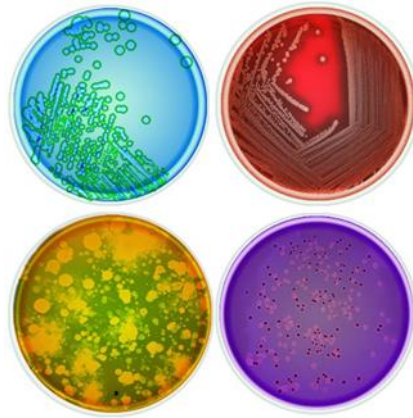
- Significant class of organic compounds
- Broad spectrum of biological activities (antiinflammatory, analgesic, antimicrobial, antitubercular, anticancer, antioxidant and so forth)
- Remarkable biological activity of azomethine metal complexes
- Important for dyes and polymers production





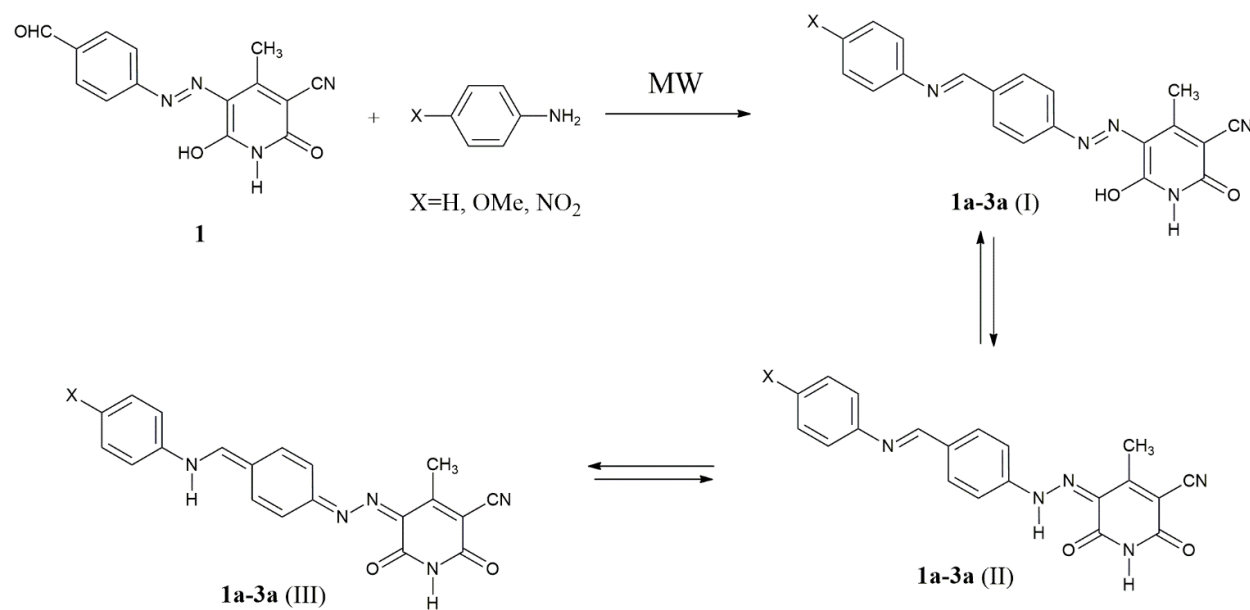
Azo-azomethine dyes

- Dyes bearing imino ($\text{CH}=\text{N}$) along with azo ($\text{N}=\text{N}$) group in the structure
- A broad range of antibacterial, antifungal, antitumor and antioxidant activities
- Application as catalysts, dyestuffs, polymer stabilizers, ligands in metal complexes, corrosion inhibitors etc.





Synthesis of azo-azomethine dyes



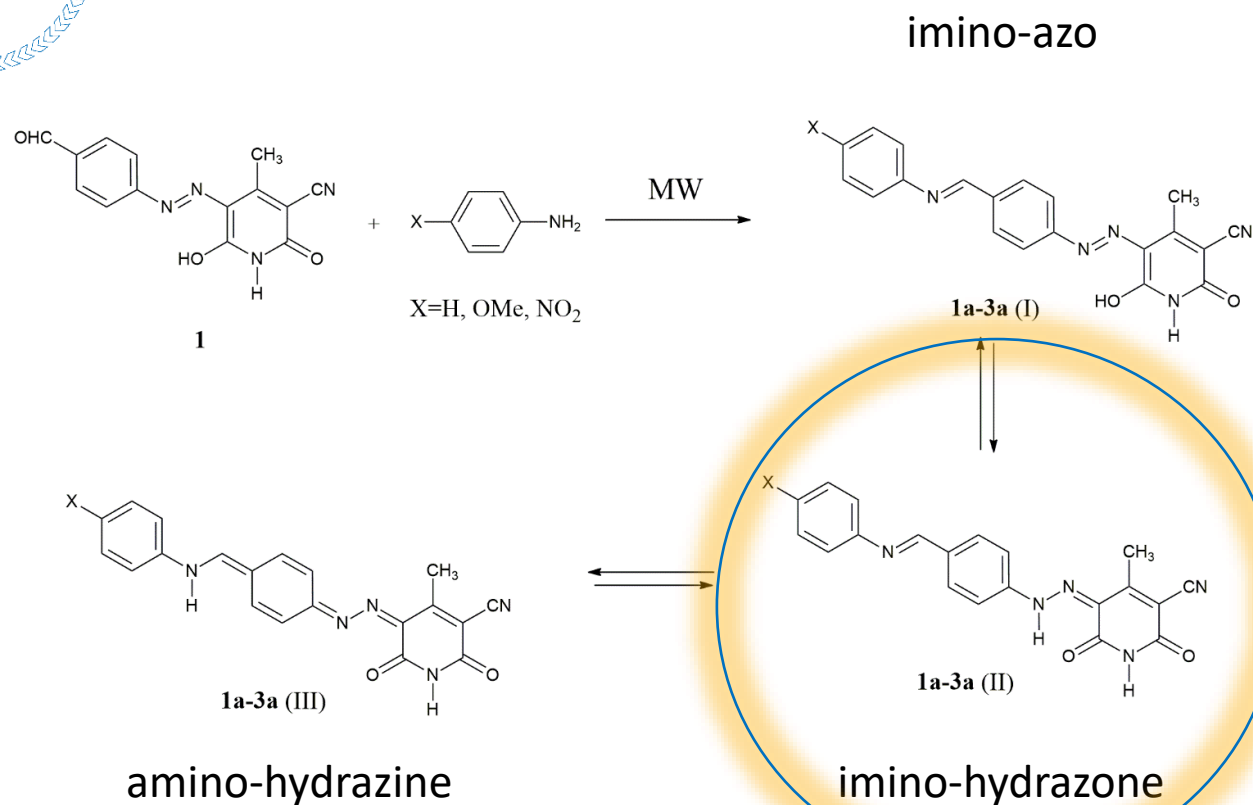
Synthetic route of azo-azomethine dyes **1a-3a**. $X = \text{H (1a), OMe (2a), NO}_2 \text{ (3a)}$.

Methods of characterization:

- M.p.
- ATR-FTIR
- NMR
- UV-Vis



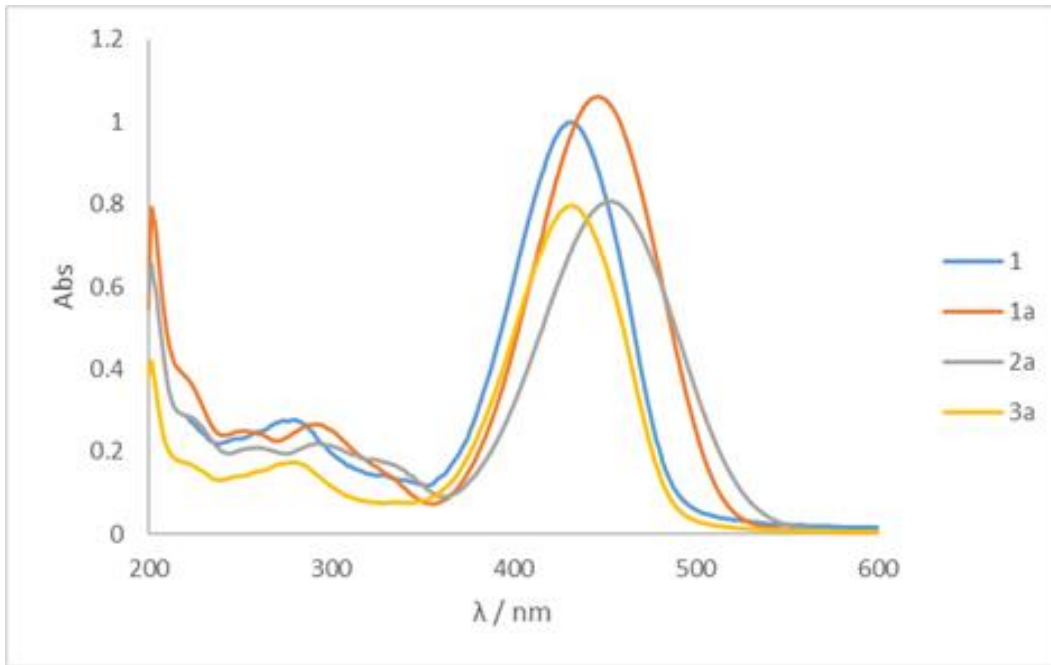
ATR-FTIR and NMR results



- Three different tautomeric forms
- The ATR-FTIR and NMR data of investigated dyes have shown the existence of imino-hydrazone form in solid state, as well as in DMSO-*d*₆ solution
- The ATR-FTIR spectra showed characteristic vibrations of N-H hydrazone group (3134-3151 cm⁻¹), two C=O carbonyl groups (1637-1646 and 1651-1660 cm⁻¹), imino C=N group (1620-1627 cm⁻¹) and cyano CN group (2117-2222 cm⁻¹).
- The signals observed at 14.60 ppm and 8.64 ppm, in the ¹H NMR spectrum of dye 1a, were ascribed to N-H hydrazone and CH=N imino group, indicating the existence of the imino-hydrazone form.



UV-Vis analysis



- Absorption maxima:
- 1 – 430 nm
- 1a – 447 nm
- 2a – 454 nm
- 3a – 432 nm

UV-Vis spectra in methanol



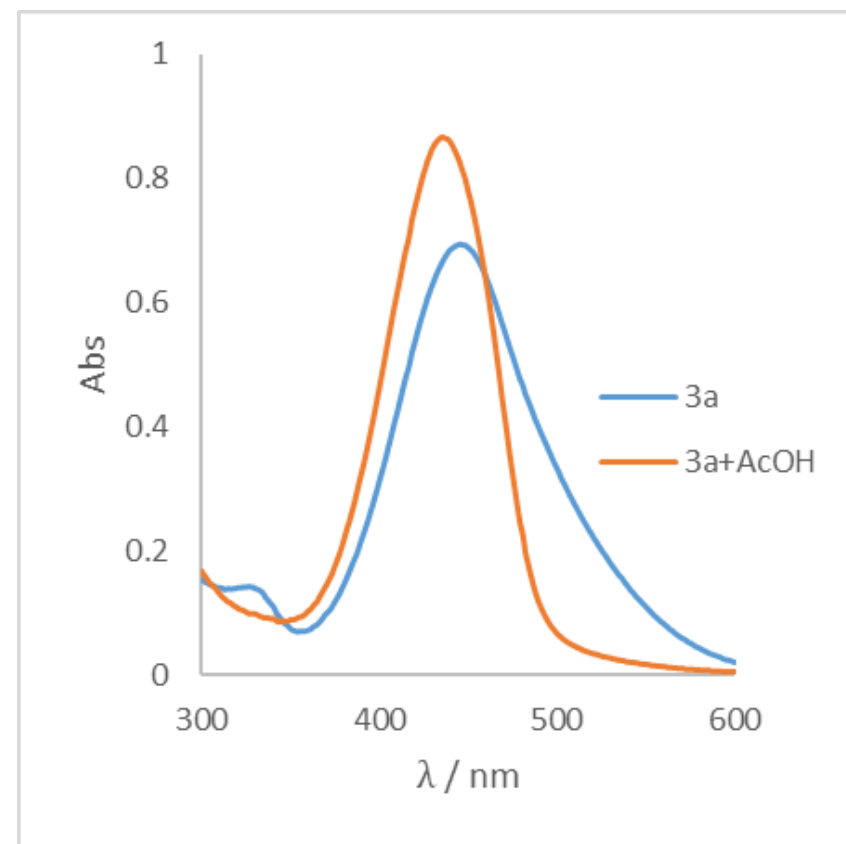
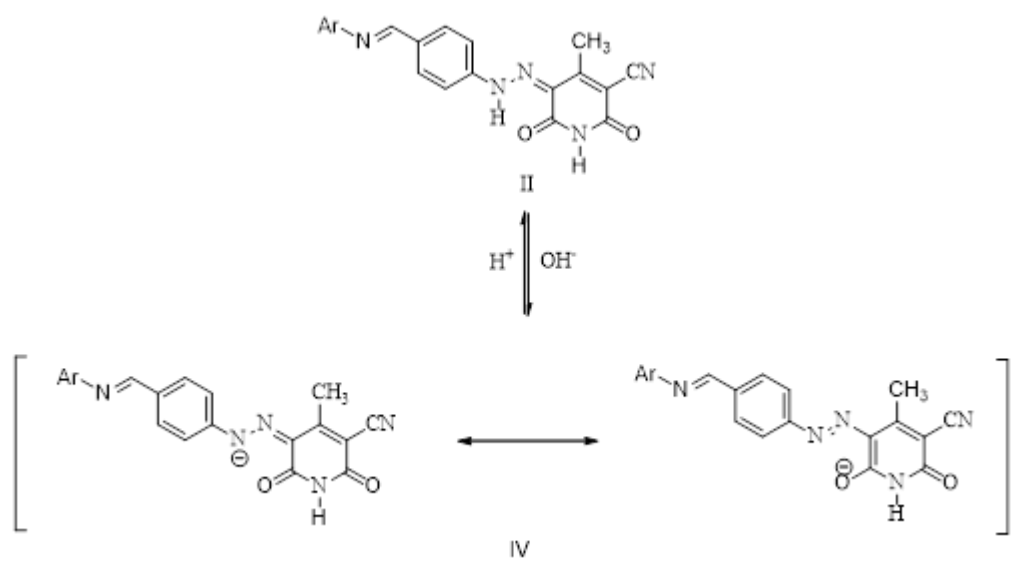
Solvatochromic properties of azo-azomethine dyes

Dye	2-Butanone	Acetonitrile	DMF	DMSO	Diethyl ether	Chloroform	Methanol	
1a	$\lambda_{\max} / \text{nm}$	446	445	449	453	442	456	447
	$\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	4.73	4.65	4.65	4.59	3.70	4.57	4.63
2a	$\lambda_{\max} / \text{nm}$	455	450	451	461	451	464	454
	$\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	4.59	4.57	4.53	4.37	3.60	4.44	4.50
3a	$\lambda_{\max} / \text{nm}$	431	431	445	440	428	437	432
	$\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	4.74	4.27	4.44	4.74	3.84	4.34	4.50

- Bathochromic shifts: DMSO and chloroform
- Hypsochromic shifts: Diethyl ether



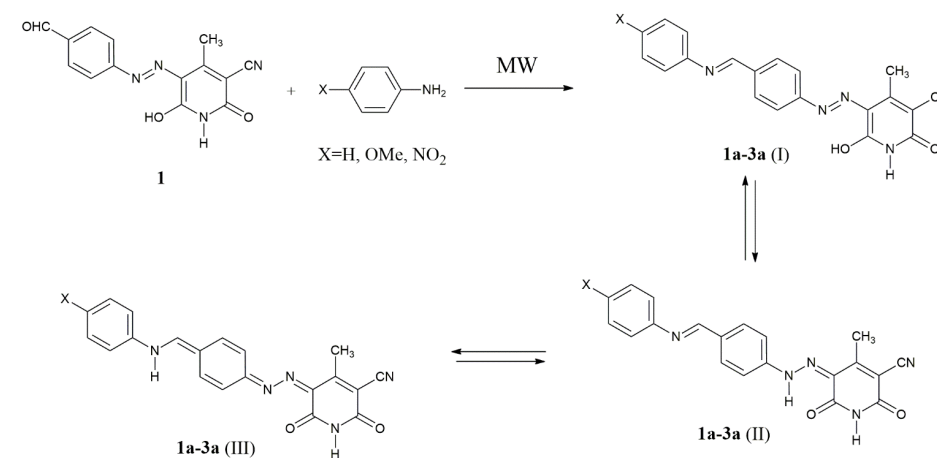
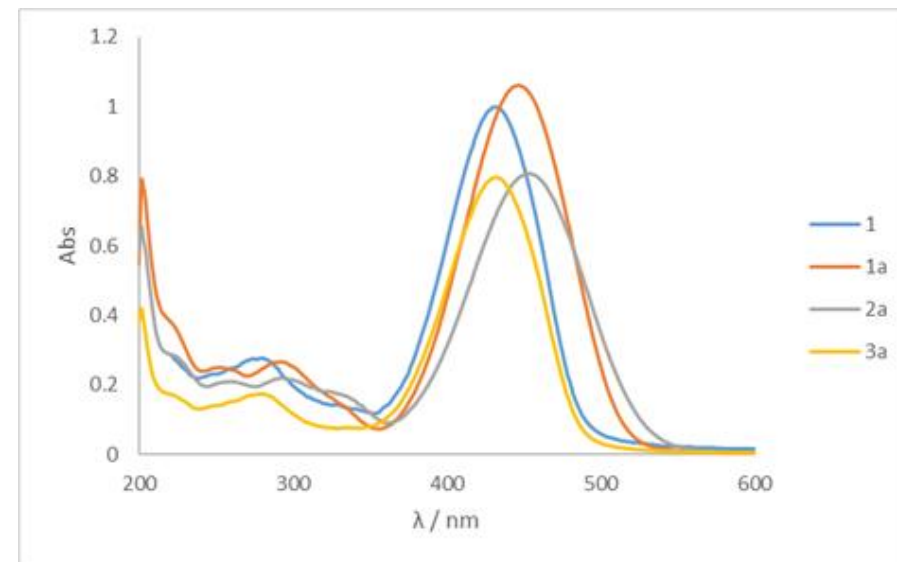
UV-Vis analysis in DMF





Conclusions

- Three novel azo-azomethine dyes have been synthesized using microwave technique
- The structures have been confirmed by ATR-FTIR, NMR and UV-Vis spectroscopies
- According to ATR-FTIR and NMR spectral data investigated dyes exist in the imino-hydrazone form
- UV-Vis analysis in methanol have shown the bathochromic shifts of absorption maxima of azo-azomethine dyes comparing to parent azo dye
- Solvatochromic properties of novel dyes have been examined in seven solvents
- In polar aprotic solvents bathochromic shifts of the absorption maxima are observed
- In non-polar solvents absorption maxima are shifted to the lower wavelengths
- In DMF solution imino-hydrazone form of the investigated azo-azomethine dyes exist at a lower wavelength than common anion





Thank you for your attention!

