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 (anti-inflammatory, 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 (CH=N) along with azo (N=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 = H (1a), OMe (2a), NO₂ (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 $^1$H 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

<table>
<thead>
<tr>
<th>Dye</th>
<th>2-Butanone</th>
<th>Acetonitrile</th>
<th>DMF</th>
<th>DMSO</th>
<th>Diethyl ether</th>
<th>Chloroform</th>
<th>Methanol</th>
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<tbody>
<tr>
<td>1a</td>
<td>$\lambda_{\text{max}}$ / nm</td>
<td>446</td>
<td>445</td>
<td>449</td>
<td>453</td>
<td>442</td>
<td>456</td>
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<td>$\epsilon$ / dm$^3$ mol$^{-1}$ cm$^{-1}$</td>
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<tr>
<td>3a</td>
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</table>

- 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!