New Ether-Azo-Anil Derivatives (Preparation, Characterization, Crystal Behavior, Solubility in Solvents)

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Abstract
New chemical compounds were prepared in our work represented ether-azo-anil compounds from types of reactions such as azotation, coupling, substitution, condensation, imination reaction to formation new organic compounds which have several applications in many fields such as organic chemistry, liquid crystal fields, and other fields. All formatted new compounds investigated by many chemical and spectral methods (FT.IR, H.NMR, Mass) – spectrophotometric, studying liquid crystals behavior for our compounds, their solubility with many solvents, physical characterization.

Keywords: etha, cry, solub.

1. Introduction
The reaction of aromatic primary amines with hydrochloric acid in azotation reaction (diazonium salt) is named diazotization\(^\text{(1-3)}\). Diazonium salts are important synthetic intermediates which undergo coupling step to form azo dyes and aromatic azo dyes, aromatic azo compounds\(^\text{(4-8)}\) tend to be brightly colored because of conjugated systems.

\[
\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} \xrightarrow{\text{aq}-\text{H}_2\text{O}} \text{NCl}^- + \text{NaCl} + \text{H}_2\text{O}
\]

Azo dyes are an important part from organic compounds, which include the coloring group (N=N-). The azo group is often bound to an aromatic system, and the dye can then be broken down to an aromatic amine, aromatic amine. Many types\(^\text{(9-16)}\) of dyes can also be broken down to aromatic amines during storage due to light and high temperature. Some aromatic amines\(^\text{(17-23)}\) have been judged to be carcinogenic.

The compounds of dyes are applied in dyeing textile fiber, cotton but also silk, wool, viscose and synthetic fiber. They are considered to be easy to use\(^\text{(24-33)}\), very cheap and to provide clear, strong colors.

The mainly of dyes are soluble in water. Azo compounds may also be toxic to aquatic organisms and cause effects in the aquatic environment., azo dyes\(^\text{(34-41)}\) are used in synthetic chemistry, as a starting material in several compounds and many fields\(^\text{(42-46)}\).
II. EXPERIMENTAL & MATERIALS

The formatted new compounds were investigated by: FT-IR spectra (FT-IR 8300 Shimadzu) in the range (400-4000) cm$^{-1}$ as KBr discs,. ¹H NMR– Spectra in DMSO–solvent,. Differential , Polarized Optical Microscope (POM). physical with chemical applications carried out for compounds.

EXPERIMENTAL PART:

STEP 1: Formation of Ether -- Anil Compounds {1}:
Para-Alkoxy benzaldehyde derivative (0.1 mole) heated with (0.1 mole) of para--methoxy aniline for (2 hrs) in ethanol and drops of glacial acetic acid according to literatures$^{(20, 24)}$, to produce precipitation, then filtered and dried, re crystallized to yield new compound {1}.

STEP 2: Formation of Ether -- Anil Compounds {2}:
Para-Alkoxy benzaldehyde derivative (0.1 mole) heated with (0.1 mole) of para--amino aniline for (2 hrs) in ethanol and drops of glacial acetic acid according to literatures$^{(20, 24)}$, to produce precipitation, then filtered and dried, re crystallized to yield new compound {2}.

STEP 3: Formation of Ether -- Anil Compounds {3}:
Compound {2} (0.1 mole) dissolved in (3 ml) of hydrochloric acid with sodium nitrite in ice temperature, then addition solution of coupling compound (meta-dinitrobenzene) according to literatures$^{(20, 24)}$, to produce precipitation, then filtered and dried, re crystallized to yield new compound {3}.

STEP 4: Formation of Ether -- Anil Compounds {4}:
Compound {2} (0.1 mole) dissolved in (3 ml) of hydrochloric acid with sodium nitrite in ice temperature, then addition solution of coupling compound (resorcinol) according to literatures$^{(210, 24)}$, to produce precipitation, then filtered and dried, re crystallized to yield new compound {4}.

STEP 5: Formation of Ether -- Anil Compounds {5}:
Compound {2} (0.1 mole) dissolved in (3 ml) of hydrochloric acid with sodium nitrite in ice temperature, then addition solution of coupling compound (para-toluic acid) according to literatures$^{(20, 24)}$, to produce precipitation, then filtered and dried, re crystallized to yield new compound {5}.

STEP 6: Formation of Ether -- Anil Compounds {6}:
Compound {2} (0.1 mole) was refluxed with maleic anhydride according to literatures$^{(20, 24)}$, to produce precipitation, then filtered and dried, re crystallized to yield new compound {6}.

Scheme 1: Synthesis of Ether -- Azo-Anil {1-4}
Scheme 2: Formation of Ether – Azo- Anil [5 , 6 ]

III.RESULTS AND DISCUSSION

Our work involved preparation of new ether-Anil – Azo compounds (1-6) which were investigated by spectral methods like ( FT-IR , H.NMR , Mass) spectra and physic - chemical studying and other applications (crystal , POM).

Chemical and Spectral Investigation:

Table (1): FT-IR data (cm⁻¹) of Compounds (1- 6 ).

<table>
<thead>
<tr>
<th>Comp</th>
<th>Other Groups</th>
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<tbody>
<tr>
<td>( 1)</td>
<td>(-C-O-C-) ether : 1236 , (CH=N) Imine group : 1619 , (CH)Aliph : 2978 .</td>
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<tr>
<td>( 2)</td>
<td>(-C-O-C-) ether : 1243 , (CH=N) Imine group : 1612 , (CH)Aliph : 2966 , (NH-) Amine : (3256 , 3247 ) .</td>
</tr>
<tr>
<td>( 3)</td>
<td>(-C-O-C-) ether : 1254 , (CH=N) Imine group : 1626 , (CH)Aliph : 2974 , (-NO2) : (1376 , 1514 ) , (-N=N-Azo : 1498 .</td>
</tr>
</tbody>
</table>

The ¹H.NMR- Investigation : showed peaks for 5 DMSO-d₆(solvent) : 2.50 (CH=H) Proton of Imine: 8.12 ,Protons of Phenyl ring: (6.74-7.59) , [CH₃-(CH₂)₃-CH₂-O -] : ( 0.61 , 0.67 , 0.69 , 0.70 , 0.72 , 0.73 ,0.94 , 0.65) in compound (1) .While compound (2) showed signals at (CH=N) Proton of Imine: 8.19 .Protons of Phenyl ring: (6.79-7.43) , [CH₃-(CH₂)₃-CH₂-O -] : ( 0.56 , 0.57 , 0.58 , 0.60 , 0.61 , 0.66 ,0.67 ) ,(-NH₂): 5 , compound(3) appeared peak at (CH=N) Proton of Imine: 8.21 .Protons of Phenyl ring: (6.74-7.59) , [CH₃-(CH₂)₃-CH₂-O -] : ( 0.61 , 0.67 , 0.69 , 0.70 , 0.72 , 0.73 ,0.94 ) , while compound (4 ) showed signals at ,(CH=N) Proton of Imine: 8.31 .Protons of Phenyl ring: (6.93-7.80) , [CH₃-(CH₂)₃-CH₂-O -] : ( 0.65 , 0.66 , 0.70 , 0.74 , 0.79 , 0.84 ,0.87 , 0.88 ) ,(OH): 11.38 . While compound (5) showed signals at ,(CH=N) Proton of
Imine: 8.24 . Protons of Phenyl ring: (6.71-7.48) ., \{CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{5}CH\textsubscript{2}-O -\} : (0.51 , 0.59 , 0.67 , 0.68 , 0.73 , 0.78 ,0.82 , 0.85) , ( COOH)Proton of carboxyl : 12. 57 ., (CH\textsubscript{3}) : 0.97 , compound (6) appeared signals at (CH=N) Proton of Imine: 8.37 . Protons of Phenyl ring: (6.95-7.55) ., \{CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{5}CH\textsubscript{2}-O -\} : (0.75 , 0.80 , 0.83 , 0.86 ,0.89 , 0.97) , (-CH\textsubscript{2}=CH\textsubscript{2} -) : (6.03 , 6.10) ., and other peaks in table (2).

Table (2): H.NMR-data (6 - ppm) of Compounds (1-6)

<table>
<thead>
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<th>Comp</th>
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<tbody>
<tr>
<td>(1)</td>
<td>DMSO-d6(solvent ) : 2.50 .,(CH=N) Proton of Imine: 8.12 .,Protons of Phenyl ring: (6.74-7.59) ., {CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{5}CH\textsubscript{2}-O -} : (0.61 , 0.67 , 0.69 , 0.70 , 0.72 , 0.73 ,0.94 , 0.65) .</td>
</tr>
<tr>
<td>(2)</td>
<td>DMSO-d6(solvent ) : 2.50 .,(CH=N) Proton of Imine: 8.19 .,Protons of Phenyl ring: (6.79-7.43) ., {CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{5}CH\textsubscript{2}-O -} : (0.56 , 0.57 , 0.58 , 0.60 , 0.61 , 0.66 ,0.67 ) , (NH\textsubscript{2}) : 5.02 .</td>
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<td>(3)</td>
<td>DMSO-d6(solvent ) : 2.50 .,(CH=N) Proton of Imine: 8.21 .,Protons of Phenyl ring: (6.74-7.59) ., {CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{5}CH\textsubscript{2}-O -} : (0.61 , 0.67 , 0.69 , 0.70 , 0.72 , 0.73 ,0.94 ) .</td>
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</tr>
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</table>

The Mass Investigation: Showed all fragments about parts of our formatted compounds in figures (1-3):

Fig(1): Mass Identification of Compound (3)

Fig(2): Mass Identification of Compound (4)
Optical Microscopic Study:
The results of optical microscopic study gave good result for behavior of crystal field for all compounds because of length and linearity\(^{41, 44}\) of our compounds. The behavior are shown in figures (4 - 9):

**Fig. 4**: Nematic Phase at 80 °C for Compound {1}

**Fig. 5**: Nematic Phase at 98 °C for Compound {2}
Fig. 6: Nematic Phase at 76 °C for Compound [3]

Fig. 7: Nematic Phase at 120 °C for Compound[4]

Fig. 8: Nematic Phase at 92 °C for Compound[5]

Fig. 9: Nematic Phase at 92 °C for Compound[6]
Solvation in Chemical Solvents:

Our formatted compounds were studied in different chemical solvents according to interaction of functional groups with solvents and solvation process, all results are abstracted in Table (3).

<table>
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<th>Table (3): Solvations of compounds in organic Solvents.</th>
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<tbody>
<tr>
<td>Compounds</td>
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<td>-----------</td>
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<tr>
<td>1</td>
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<td>6</td>
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REFERENCES


