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Synthesis of azo dyes based on N-phenyl maleimide derivatives

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ABSTRACT

The azo dyes (A1-9) was synthesized based on the N-phenyl maleimides derivatives by the reaction with 4-aminoantipyrine, the first reaction is synthesis of amic acids after that dehydration of water to yield the maleimides (M1-9), the synthesized compounds tested by the FT-IR and UV-VIS. spectroscopic techniques.

Keywords: Azo compounds, 4-aminoantipyrine, maleimide, amic acid.

INTRODUCTION

Azo compounds, which were developed in the mid 1800s, are one of the most common dye materials and are useful synthetic intermediates, where representing 60 - 80% of all organic colorants[1,2], the azo compound use in wide range of applications, and applied in many different industries, including the textiles, paper, cosmetic, leather, food and pharmaceutical industries[3]. The N=N group is called an azo or diimide functional group, and when found aromatic group in molecule this helps to stabilize the N=N group by making it a part of an extended delocalized system. This lead to making azo compounds colored, and the molecules absorb visible frequencies[4,5].

The molecules which have imide groups exhibit great electrical properties, good solubility in polar media, resistance to hydrolysis and high thermal stability[6]. Maleimides are an important class of substrates for biological, pharmacological and chemical applications[7,8]. Many methods used to synthesis of maleimides, by dehydration of water molecule form amic acids such as using of acetic anhydride and sodium acetate[9], by using the molting method[10], by crushing heat method to malic acid salt[11], by Diels-Alder reactions[8], by phase transfer catalysis[12], and by using trifluoroacetic acid[13].

In the past twenty years, heterocyclic coupling agents received a great deal of attention because of their excellent properties which are light fastness, good substantivity, good migration and have a very brilliant shade[14]. Antipyrine derivatives are well known compounds used mainly as analgesic and antipyretic drugs, one of the best known antipyrine derivatives is 4-aminoantipyrine which is used for the protection against oxidative stress as well as prophylactic of some diseases including cancer and these are important directions in medicine and biochemistry[15,16].

MATERIALS AND METHODS

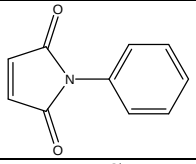
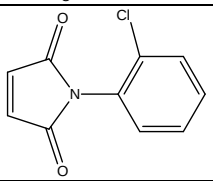
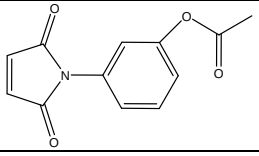
Chemical materials which used in this work were purchased from Fluka, BDH, and Himedia. And the instruments which used melting point measurement is Electro thermal melting point Stuart Model SMP30, IR spectroscopy analyses were recorded on Schimadzu FTIR 8400S spectrometer in 4000 – 200 cm-1 range using KBr pellet, The UV-Visible spectra were recorded on UV-1650PC Spectrophotometer Shumadzu in the wave length range 200 - 800 nm.

Procedure for synthesis amic acids : The method used same in literature [17] with some modification, where equal mols from maleic anhydride or malic anhydride and substituted aniline was dissolved in acetone or diethyl ether and the aniline by ethanol, and then the anhydrides was added drop wise to aniline solution and string for 2-2.5 h, after that the precipitate was filtered and dry, then recrystallized by dissolving in sodium bicarbonate solution, the solution filtered and precipitated by adding hydrochloric acid solution and filtered and washed by ethanol, then by ether and dried.

Procedure for synthesis maleimides (M1-9): The same method was used as in literature [9] with some modification, where amic acid derivatives were dissolved in acetic anhydride and added anhydrous sodium acetate (10% - 20%) by weight, the mixture was refluxed on water bath until the color was changed, then cooled the solution and poured in ice bath with vigorously stirring, where the maleimide is precipitated. Precipitate filtered and washed with sodium bicarbonate solution and dried and recrystallized with suitable solvent.
The same procedure was used for the synthesis of malimides (M9).

Procedure for synthesis of azo compound (A1-9): The same method was used as in literature [6] with some modification, where solution A was prepared by mixing 4-aminoantipyrine (0.01 mol) with concentrated HCl (3 mL) and water (3 mL) and cooling at 5 °C in an ice bath. $NaNO_2$ (0.01 mol) was dissolved in water (10 mL) at 5 °C to obtain solution B. Then solution A was added drop wise to solution B at 5 °C with stirring. The mixture was then slowly added into the solution of maleimides (0.01 mol), which was dissolved in 10% NaOH (20 mL) at 5 °C. The mixture was keep chilled in the ice bath and stirred continuously for 10 min. The solution then acidified with hydrochloric acid solution to neutralize. The precipitate was filtered and dried, then recrystallized with suitable solvent.The tables 1and 2 show the physicals properties maleimides and azo compounds respectively.

Table 1. The physicals properties of maleimides.

Comp No.	Structures	M.F	M.wt (gm/mole)	Yield%	M.P (°C)	
M1		$C_{10}H_7NO_2$	173	85	86	Green
M2		$C_{10}H_6ClNO_2$	207	61	56	Gray
M3		$C_{12}H_9NO_4$	231	65	oil	Nutty

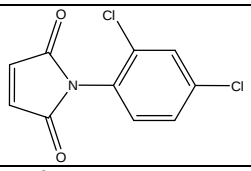
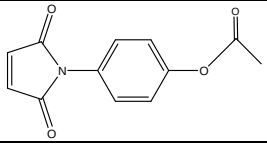
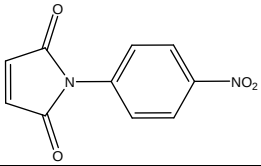
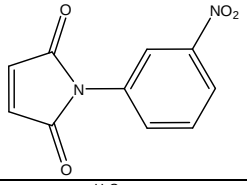
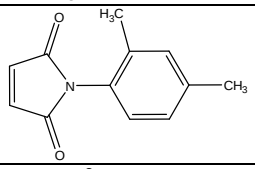
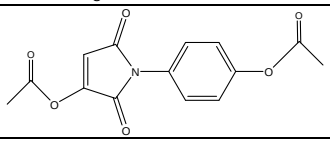
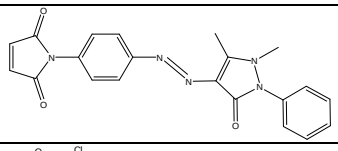
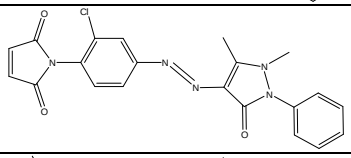
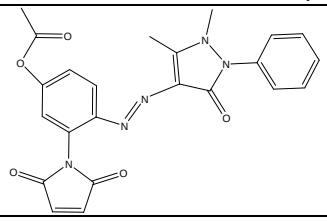
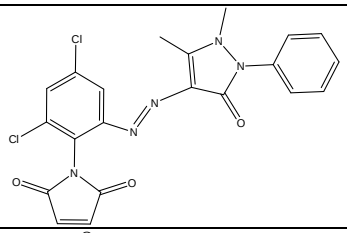
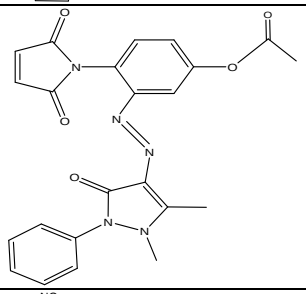
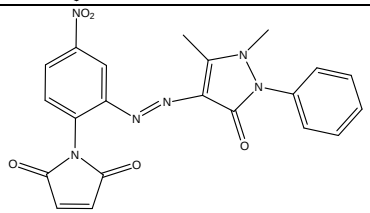
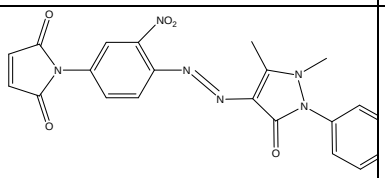
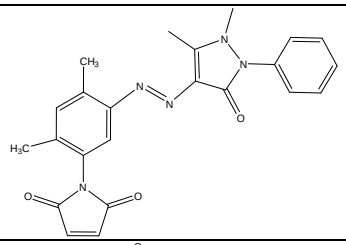
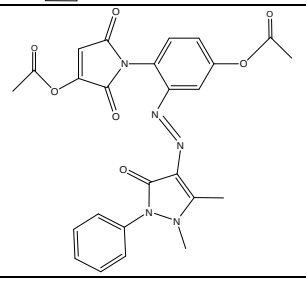
M4		$C_{10}H_5C_{l2}NO_2$	242	66	108	Gray
M5		$C_{12}H_9NO_4$	231	67	165	Green
M6		$C_{10}H_6N_2O_4$	218	89	145	Light Brown
M7		$C_{10}H_6N_2O_4$	218	83	122	Violet
M8		$C_{12}H_{11}NO_2$	201	80	52	Sliver
M9		$C_{14}H_{11}NO_6$	289	81	107	Green

Table 2. The physicals properties of azo compounds.

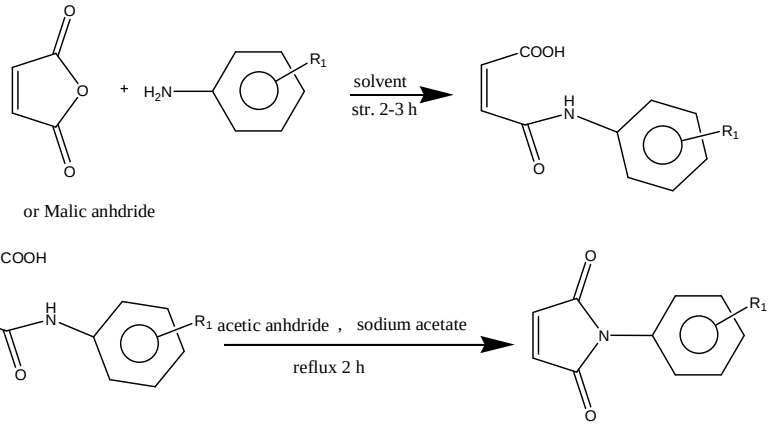
Comp No.	Structures	M.F	M.wt (gm/mole)	Yield %	M.P (°C)	Color
A1		$C_{21}H_{17}N_5O_3$	387	68	209	Pale nutty
A2		$C_{21}H_{16}ClN_5O_3$	421	57	220	Brown
A3		$C_{23}H_{19}N_5O_5$	445	56	210	Dark brown

A4		$C_{21}H_{15}Cl_2N_5O_3$	456	47	136	Pale brown
A5		$C_{23}H_{19}N_5O_5$	445	64	130	Brown
A6		$C_{21}H_{16}N_6O_5$	432	42	178	Brown
A7		$C_{21}H_{16}N_6O_5$	432	51	185	Pale brown
A8		$C_{23}H_{21}N_5O_3$	415	60	106	Brown reddish
A9		$C_{25}H_{21}N_5O_7$	503	74	155	Nutty

RESULTS AND DISCUSSION

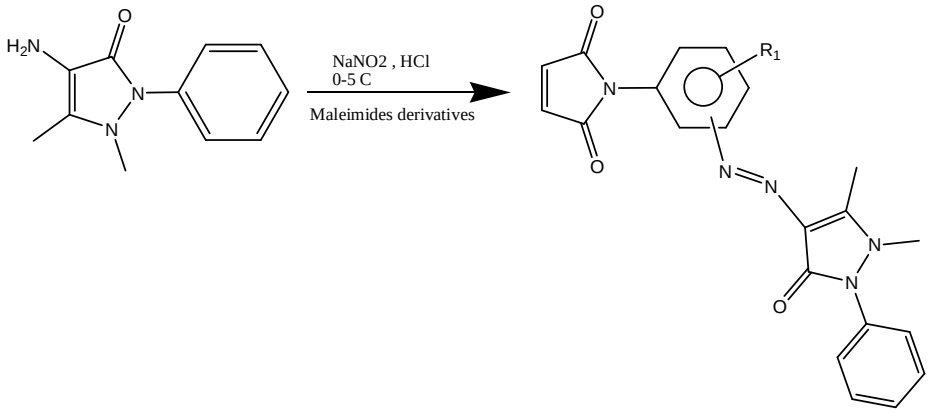
In this work was prepared amic acids and then flowed by the dehydration of it to maleimides (M1-9), the azo compound (A1-9) synthesized by the reaction of 4-aminoantipyrine with N-phenyl maleimide, this molecules was identified by the FTIR spectrum and UV-Vis. spectrum.

The reaction routes for the synthesis process of amic acids then maleimides.



	A1	A2	A3	A4	A5	A6	A7	A8	A9
R1	H	2-Cl	3-Ac	2,4-Cl	4-Ac	4-NO2	3-NO2	2,4-methyl	4-Ac

The reaction of azo dyes synthesis.



The essential data of FTIR show in the below tables 3 and 4

Table 3. The mean FT-IR frequencies of maleimide.

No.	υ (=C-H) str. olefine	υ(=C-H) cis. ben.	υ(C=O) str.	υ(C-N)	υ(C=C) str. Ar.	υ (=C-H) str. Ar.	υ(C-H) inplane	υ(C-H) oop	note
M1	3093	698	1712	1205	1593 1500	3093	1149 1070	831	
M2	3094	678	1716	1213	1585 1485	3094	1153 1062	827	715 υ (C-Cl)
M3	3091	685	1705	1213	1589 1515	3091	1152 1045	825	2970 υ(-C-H) alkan
M4	3097	686	1718	1217	1585 1538	3097	1153 1055	831	715 υ(C-Cl)
M5	3095	687	1706	1213	1590 1505	3095	1150 1099	850	1748 υ(C=O) ester 2975 υ(-C-H) alkan
M6	3099	644	1724	1217	1599 1504	3099	1146 1059	854	1531,1344 υ(N-O)
M7	3101	694	1724	1217	1581 1512	3101	1143 1093	734	1537,1348 υ(N-O)
M8	3081	682	1717	1232	1652	3081	1151	827	2927

					1503		1026		υ(-C-H) alkan
M9	3095	687	1707	1213	1590 1505	3095	1150 1099	825	1748 υ(C=O) ester 2970 υ(-C-H) alkan

Table 4.The mean FT-IR frequencies of azo dyes.

No.	υ(=C-H) str. olefine	υ(=C-H) cis. ben.	υ(C=O) str.	υ(-N=N-)	υ(C-N)	υ(C=C) str. Ar.	υ(=C-H) str. Ar.	υ(C-H) inplane	υ(C-H) oop	note
A1	3061	698	1670	1495	1309	1591 1529	3061	1139 1022	759	2927 υ(-C-H) alkan
A2	3064	693	1727	1488	1306	1590 1526	3064	1157 1022	754	725 υ(C-Cl) 2960 υ(-C-H) alkan
A3	3059	608	1695	1494	1296	1591 1529	3059	1126 1014	756	2937 υ(-C-H) alkan
A4	3094	684	1717	1484	1300	1588 1520	3094	1150 1054	828	756 υ(C-Cl) 2993 υ(-C-H) alkan
A5	3041	693	1719	1490	1369	1591 1513	3041	1157 1021	752	2950 υ(-C-H) alkan
A6	3087	688	1705	1495	1307	1595 1511	3087	1110 1047	825	1553,1333 υ(N-O) 2910 υ(-C-H) alkan
A7	3099	735	1714	1487	1354	1589 1527	3099	1240 1092	853	1550,1354 υ(N-O) 2879 υ(-C-H) alkan
A8	3022	689	1712	1494	1376	1592 1440	3022	1244 1151	827	2972 υ(-C-H)
A9	3061	694	1713	1498	1269	1546 1645	3061	1197 1018	840	2933 υ(-C-H) alkan

From this data we can see that when imide form from amic, the frequency of stretching vibration of N-H and O-H bonds disappears and also the frequency of stretching vibration of the C=O group was shifting to large frequency because the formation of imide group.

The FT-IR spectrum indicates that the azo dyes has successfully undergone the azo coupling reaction, as can be seen from the absorption by the azo functional group (-N=N-) frequency of stretching vibration in the (1484-1498)cm^{-1} region, which can't found in the maleimides charts. The comparison of IR values between tables 3and4 we can see that there appears the frequency of stretching vibration of C-H (2879-2993) cm^{-1} for methyl group of antipyrine.

UV-Vis spectrum of azo compound is shown in table 5. Azo functional group (-N=N-) usually give its absorption wavelength in the range from 350 nm-370 nm[14]. This absorption due to the $n \rightarrow \pi^*$ transitions for this group and carbonyl group, and this indicate to the formation of the azo compounds, the shift of the value to up because the bathochromic shifts which result from the polar solvent (methanol) which used in solvent of dyes[18].

Table 5. Electronic spectral data (λ max of azo-dyes).

Comp. No.	Wavelength (nm)	Wavelength (nm)
A1	381.5	324
A2	380	322
A3	385	320
A4	381	318
A5	377	321
A6	384	323
A7	379	319
A8	378	317.5
A9	375	325

APPLICATIONS

The synthesized compounds can used in the dyes industries, and can use in the synthesis of polymers as homopolymers and copolymers which useful in many of industries.

CONCLUSIONS

The compounds can using in the polymerization reactions in both types homo and copolymerization with vinyl compounds by using the AIBN initiator. And also can using in reaction with thiols by the carbon-carbon double bond and other reactions.

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