

Synthesis and characterization of some new substituted azo-coumarin and schiff's bases

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ABSTRACT

A series of new Azo-coumarins and Schiff's bases were synthesized by the condensation of 2-methoxy-5-methyl phenyl Azo-salicylaldehyde with different substituted phenyl malon-anilic acids by using pyridine as a catalyst. The structures of newly synthesized compounds have been characterized on the basis of elemental analysis, spectral studies like IR and their physical properties.

Key words : Substituted Azo-salicylaldehyde, Malon-anilic acids, & Schiff's bases, Spectral studies.

INTRODUCTION

Azo Compounds have received much attention and have been widely used in many practical applications such as colouring fiber, printing systems and analytical chemistry. Heterocyclic azo-coumarins attract considerable interest and an important role in the development of the chemistry of azo compounds. In this class of some azo-coumarin have been reported to inhibit tumor growth in mice and rats¹, azo-coumarins have also been reported to possess anti-allergic², anti-coagulant³, anti-diabetic⁴, analgesic⁵ properties. Schiff's bases have also possess antiviral⁶, anticancer⁷, anti-bacterial⁸ activities. Several Azo-coumarins & Schiff's bases have been prepared in our laboratory⁹⁻¹³. As a continuation of our previous studies on the synthesis of azo-coumarin & Schiff's bases. Herein the present study we have synthesized a series of new methoxy and methyl substituted azo-coumarin & Schiff's bases.

In this paper, we report the condensation of 2-methoxy-5-methyl phenyl Azo-salicylaldehyde with different malon-anilic acids in the presence of a trace of pyridine as a condensing agent.

EXPERIMENTAL

Material

All the melting points determined in open Capillary tubes on an electro-thermal apparatus and were uncorrected. All the chemicals are used in the synthesis were obtained from Sigma-Aldrich company. The newly synthesized compounds were recrystallised by Absolute ethanol. The purity of all the newly synthesized compounds were routinely checked by TLC on silica-gel Al Plates (E-Merck), by using 10% benzene/methanol for azo-coumarins and Schiff's bases by using 5% benzene/methanol.

IR spectra in KBr were recorded on a Perkin – Elmer spectrum RX-1 FT-IR spectro-

photometer at St. John's College Agra. The selected physical and characteristic data of the synthesized compounds were listed in Table-1.

Synthesis of 2-hydroxy-5(2-methoxy-5-methyl phenyl azo) benzaldehyde (1a)

To the substituted amine (2-methoxy-5-methyl; 0.025 mole) was diazotised by adding concentrated HCl (8ml) in 7ml distilled water maintaining temperature at 0°C in an ice-bath, after that the cold solution of sodium nitrite in water (8ml) was added at 0°C-2°C temperature till the reaction was complete, then a solution of salicylaldehyde (0.025mole) in 2N NaOH (20ml) was added to the above diazotised solution with constant stirring. The solid obtained was filtered, washed with cold distilled water and dried, recrystallised by hot ethanol, yield 44.26 %.

Synthesis of N (R) - phenyl malon - anilic acid (2a-2j)

To the primary aniline (0.025 mole), diethyl malonate (0.05 mole) was added with a catalyst dimethyl formamide and refluxed for about 45-60 minutes, after cooling, to the filtrate ethanol (20 ml) and a solution of Na₂CO₃ (20 ml) was added to it hydrolysis taken for about 30-45 minutes and then filtered, to the filtrate concentrated HCl was added dropwise with constant stirring. The solid thus separated was filtered washed with distilled

water and recrystallised the compound with sat. solution of NaHCO₃ was identified as N-(R)-phenyl malon-anilic acid (2a-2j).

Synthesis of 6 (phenyl azo)-coumarin-3-carboxy-2-methoxy-5-methyl anilide (3a-3j) and 2- hydroxy-5 (phenyl azo)-benzylidine-2-methoxy-5-methyl aniline (4a-4j)

A mixture of 2-hydroxy-5(2-methoxy-5-methyl phenyl azo) benzaldehyde (1a; 0.001 mole) and N(R)-phenyl malon-anilic acid (2a-2j; 0.001 mole), with a trace of pyridine was added to it, then the reaction mixture was heated for 4-hours in an oil-bath maintaining the temperature 104° to 112°, the mixture melted to a liquid and then set to a solid, after cooling it was digested with the solution of NaHCO₃ and then washed with distilled water several times. The Schiff's bases was removed by extraction with hot ethanol (12 ml) and then the residue was recrystallised from absolute ethanol and also the schiff's bases was recrystallised from absolute ethanol.

RESULTS AND DISCUSSION

The IR Spectra in KBr of the newly synthesized compounds have been recorded in the frequency region 4000-450 cm⁻¹, the IR spectral data are recorded in Table 2.

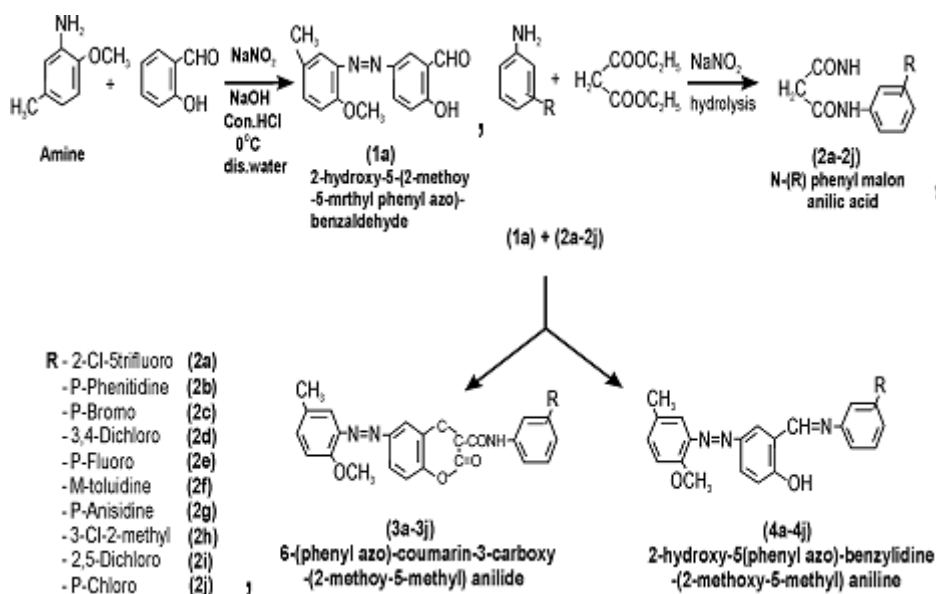


Table 1 : Physical & Analytical data of synthesized Compounds (1a,2a-2j,3a-3j,4a-4j)

S. No.	Compounds code	Molecular Formula	Molecular Weight	Melting Point 0°C	Yield %	Colour	C		H		N	
							cal.%	(Found)	cal.%	(Found)	cal.%	(Found)
1.	1a	C ₁₆ H ₁₅ N ₃ O ₃	271.30	84°	44.26	sunrise	66.40	(66.43)	5.57	(5.59)	10.32	(10.33)
2.	2a	C ₁₀ H ₇ N ₃ O ₃ Cl ₁ F ₃	281.63	132°	43.24	light green	42.64	(42.68)	2.50	(2.51)	04.97	(04.99)
3.	2b	C ₁₁ H ₉ N ₃ O ₄	223.23	133°	62.22	crystalline suede	59.18	(59.20)	5.87	(5.89)	06.27	(06.29)
4.	2c	C ₉ H ₇ N ₃ O ₃ Br ₁	258.06	138°	57.09	white	41.88	(41.91)	3.12	(3.13)	05.43	(05.45)
5.	2d	C ₉ H ₇ N ₃ O ₃ Cl ₂	248.06	121°	60.14	sandal wood	43.57	(43.58)	2.84	(2.86)	05.64	(05.66)
6.	2e	C ₉ H ₇ N ₃ O ₃ F ₁	197.16	142°	53.14	crystalline white	54.82	(54.85)	4.09	(4.10)	07.10	(07.13)
7.	2f	C ₁₀ H ₁₁ N ₃ O ₃	193.20	82°	47.10	crystalline white	62.16	(62.18)	5.74	(5.75)	07.25	(07.27)
8.	2g	C ₁₀ H ₁₁ N ₃ O ₄	209.19	136°	45.34	lavender dew	57.41	(57.43)	5.29	(5.31)	06.69	(06.71)
9.	2h	C ₁₀ H ₁₀ N ₃ O ₃ Cl ₁	227.65	129°	43.76	dirty white	52.76	(52.78)	4.42	(4.44)	06.15	(06.18)
10.	2i	C ₉ H ₉ N ₃ O ₃ Cl ₂	248.06	153°	54.84	jasmine	43.57	(43.60)	2.84	(2.85)	05.64	(05.66)
11.	2j	C ₉ H ₉ N ₃ O ₃ Cl ₁	214.51	139°	50.54	coral shell	50.81	(50.84)	3.76	(3.77)	06.53	(06.55)
12.	3a	C ₂₅ H ₁₈ N ₃ O ₄ Cl ₁ F ₃	516.09	237°	35.50	bricktone	58.09	(58.12)	3.51	(3.53)	08.13	(08.16)
13.	3b	C ₂₆ H ₂₀ N ₃ O ₅	458.50	198°	46.76	dark orange	68.11	(68.13)	5.27	(5.28)	09.16	(09.18)
14.	3c	C ₂₆ H ₁₉ N ₃ O ₄ Br ₁	493.35	217°	41.51	dirty yellow	58.43	(58.45)	3.88	(3.90)	08.52	(08.53)
15.	3d	C ₂₆ H ₁₉ N ₃ O ₄ Cl ₂	483.34	205°	51.63	dull yellow	59.64	(59.65)	3.75	(3.76)	08.69	(08.70)
16.	3e	C ₂₆ H ₁₉ N ₃ O ₄ F ₁	432.44	214°	39.95	light sunset	66.66	(66.69)	4.43	(4.45)	09.72	(09.74)
17.	3f	C ₂₆ H ₂₂ N ₃ O ₄	428.47	187°	38.79	golden yellow	70.08	(70.10)	5.17	(5.16)	09.81	(09.83)
18.	3g	C ₂₆ H ₂₂ N ₃ O ₅	444.47	196°	51.66	geranium	67.55	(67.58)	4.99	(4.97)	09.45	(09.48)
19.	3h	C ₂₅ H ₂₁ N ₃ O ₄ Cl ₁	462.92	231°	36.54	orangish yellow	64.86	(64.88)	4.57	(4.58)	09.08	(09.10)
20.	3i	C ₂₆ H ₁₉ N ₃ O ₄ Cl ₂	483.34	224°	46.05	dark yellow	59.64	(59.66)	3.75	(3.76)	08.69	(08.70)
21.	3j	C ₂₆ H ₁₉ N ₃ O ₄ Cl ₁	448.90	222°	54.63	mild sunset	64.21	(64.22)	4.26	(4.28)	09.36	(09.37)
22.	4a	C ₂₂ H ₁₉ N ₃ O ₂ Cl ₁ F ₃	449.87	102°	36.77	brown	58.73	(58.75)	4.26	(4.27)	09.34	(09.36)
23.	4b	C ₂₈ H ₂₃ N ₃ O ₃	391.48	99°	40.08	rust	70.56	(70.59)	6.44	(6.46)	10.73	(10.75)
24.	4c	C ₂₁ H ₂₀ N ₃ O ₂ Br ₁	426.33	82°	37.05	light coffee	59.16	(59.18)	4.73	(4.75)	09.86	(09.87)
25.	4d	C ₂₁ H ₁₉ N ₃ O ₂ Cl ₂	416.32	84°	44.50	african red	60.59	(60.58)	4.60	(4.61)	10.09	(10.08)
26.	4e	C ₂₁ H ₂₀ N ₃ O ₂ F ₁	365.41	94°	42.09	light brown	69.03	(69.01)	5.52	(5.53)	11.50	(11.49)
27.	4f	C ₂₂ H ₂₃ N ₃ O ₂	361.45	sticky	36.20	light coffee	73.00	(73.08)	6.14	(6.13)	11.62	(11.64)
28.	4g	C ₂₂ H ₂₃ N ₃ O ₃	377.45	sticky	46.04	satin brown	70.00	(70.02)	6.14	(6.15)	11.13	(11.15)
29.	4h	C ₂₂ H ₂₂ N ₃ O ₂ Cl ₁	395.90	78°	39.55	brown	66.74	(66.76)	5.60	(5.62)	10.61	(10.62)
30.	4i	C ₂₁ H ₁₉ N ₃ O ₂ Cl ₂	416.32	101°	41.81	satin brown	60.59	(60.62)	4.60	(4.61)	10.09	(10.12)
31.	4j	C ₂₁ H ₂₀ N ₃ O ₂ Cl ₁	381.87	90°	42.88	coffee	66.05	(66.08)	5.28	(5.29)	11.06	(11.08)

Table 2: IR asorption bands

Compounds code	-OHcm ⁻¹ stretching	HC=N cm ⁻¹ stretching	Lactone stretching	-CONH cm ⁻¹ stretching	Ar C=C cm ⁻¹ stretching	N=N cm ⁻¹ stretching	C-Cl cm ⁻¹ stretching	N-H cm ⁻¹ stretching
1a	3430	-	-	-	-	1459.3	691.8	-
3a	-	-	1718.2	1667.1	1588.5	1426.9	671.6	3469.8
3b	-	-	1703.3	1662	1548.8	1464.6	666.8	3468
3c	-	-	1706.8	1598.4	1546.8	1455	670.7	3455
3d	-	-	1706.7	1592.4	1533.3	1426.1	670.6	3465
4a	3410.6	2361.0	-	-	1504.9	1428.9	670.2	-
4b	3420	2362.0	-	-	1509.4	1414.1	669.0	-
4c	3435	2343.5	-	-	1566.5	1428.7	668.7	-
4d	3433	2343.3	-	-	1530.7	1429.3	669.5	-

The IR spectrum of 2-hydroxy-5-(2-methoxy-5-methyl) phenyl azo benzaldehyde^{1a} shows absorption at 3430 cm⁻¹ reveals free -OH group stretching vibrations, absorption at 1459.3 cm⁻¹ reveals -N=N stretching vibrations, absorption at 691.8 cm⁻¹ indicating -C-Cl stretching vibrations.

Thus the IR spectral results of the compound provided the direct information about the presence of azo group and characters lent support to the structure of compound no. 1a.

The infrared spectra of 6(2-chloro-5-trifluoro methyl phenyl azo)-coumarin-3-carboxy-(2-methoxy-5-methyl)anilide^{3a} shows absorption at 3469.8 cm⁻¹ indicates the presence of -NH stretching vibrations, absorption at 1718.2 cm⁻¹ reveals -C=O stretching vibrations, absorption at 1667.1 cm⁻¹ indicates the presence of -CONH stretching vibrations, absorption in the range 1588.5 cm⁻¹ indicates the presence of aromatic -C=C, absorption at 1426.9 cm⁻¹ indicates -N=N stretching vibrations, absorption at 671.6 cm⁻¹ indicating the -C-Cl stretching vibrations. Thus the Infrared spectral results of these characters are support to the structure of compounds no.3a,3b-3d and other compounds (3e-3j).

The Infrared spectra of 2-hydroxy-5-(2-chloro-5-trifluoro methyl) benzylidene-(2-methoxy-5-methyl)aniline^{4a}, shows absorption at 3410.6 cm⁻¹ reveals -OH stretching vibrations, absorption at 2361 cm⁻¹ indicates -HC=N stretching vibrations, absorption in the range 1504.9 cm⁻¹ indicates the aromatic character of -C=C, absorption at 1428.9 cm⁻¹ shows -N=N stretching vibrations, absorption at 670.2 cm⁻¹ indicates -C-Cl stretching vibrations. Thus the infrared spectral results of above compound are agreed the assigned structure of compound no.4a,4b-4d and other compounds (4e-4j).

Thus the infrared spectral data of all the substituted azo-coumarins and Schiff's bases are indicating the absorption spectrum was in agreement with assigned structure. The azo-coumarins were found to possess higher melting points as compared to Schiff's bases which melted at lower melting points.

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