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Spectroscopic Characterization of Some Chromone Azo Dyes

Y.M. ISSA*, A.L. EL-ANSARY, O.E. SHERIF and M.M. EL-AJILY
Department of Chemistry
Cairo University, Faculty of Science, Giza, Egypt

Chromone azo dyes of 6-formyl-7-hydroxy-5-methoxy-2-methylchromone (I), 5,7-dihydroxy-6-formyl-2-methylchromone (II) and 5,7-dihydroxy-2,6-dimethylchromone (III) were prepared. The chromone azo dyes were characterized by elemental analysis, IR, ^{1}H NMR and mass spectra. IR and ^{1}H NMR indicate the presence of hydrogen bond between hydroxyl group in position seven and the formyl group in position six (Ia–Id). Also a hydrogen bonding between a hydroxyl group in position five and the chromone carbonyl in position four is possible (IIa–d and IIIa–d). The mass spectra indicate that molecular ions of some chromone azo dyes were highly unstable, while the molecular ion was observed in other cases. The fragmentation patterns indicate retro Diels-Alder reaction in some cases.

INTRODUCTION

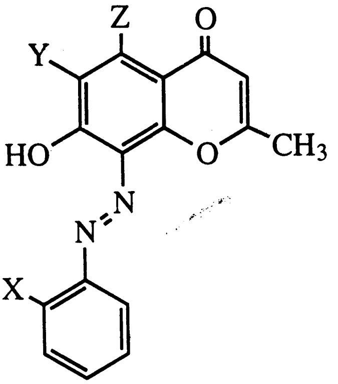
Most of naturally occurring chromones contain alkoxyl or hydroxyl group.[1] Hydroxychromones have been widely used as analytical reagents for spectrophotometric determination of metal ions.[2, 3] Some chromone derivatives have marked analgesic effect. They have been used for the relief of spasms of the ureter, gall bladder and in bronchial asthma.[4–7] Syntheses of naturally occurring 5-methylchromones were reported.[8] The syntheses of certain 8-arylazo as well as phenylhydrazones, 7-alkoxy and acyloxychromone derivatives was described.[9] El-Ansary[10] prepared some chromone containing azo dyes. The ionization constants of the dyes were determined potentiometrically and spectrophotometrically. The IR spectra of the compounds have been investigated and discussed.

The present study deals with the spectroscopic study and characterization of some new azo dye derivatives containing chromone moieties. The compounds were investigated using elemental analyses, IR, NMR and mass spectrometry.

EXPERIMENTAL

All chemicals and reagents used in this investigation were chemical pure grade from BDH and Aldrich. The chromone derivative, 6-formyl-7-hydroxy-5-methoxy-2-methyl-chromone (I) was prepared by oxidation of visnagin with chromic acid, while 5,7-dihydroxy-6-formyl-2-methylchromone (II) was prepared by hydrolysis of compound (I) with HCl and 5,7-dihydroxy-2,6-dimethylchromone (III) was prepared by reduction of compound (II) with Zn, as recommended by Schonberg *et al.*[11]

The melting points of the resulting chromones (I, II and III) were 189°C (lit. 189°C), 194°C (lit. 195°C) and 286° C dec. (lit. 287°C dec.), respectively. The chromone azo dyes were propared by coupling of the corresponding diazonium salts (prepared in the usual manner)[12] with the chromone in presence of NaOH as recommended.[12] The product was acidified with dilute hydrochloric acid (1 : 1) until pH 2–4, then filtered and washed with distilled water, dried and recrystallized from suitable solvent till constant melting point (Table-1). Elemental analyses were carried out at Microanalytical Center, Cairo University, using Perkin-Elmer 2400 elemental analyzer. The resulting chromone azo dyes have the following structural formula:



No.	Z	Y
I	OCH_3	CHO
II	OH	CHO
III	OH	CH_3

X = H (a), OH (b), COOH (c) and $AsO(OH)_2$ (d)

The IR spectra were recorded as KBr discs using Perkin-Elmer 1430 and Pye-Unicam SP 3–300 infrared spectrometers. The ^1H NMR spectra were carried out using Varian Gemini 200–200 MHz spectrometer. The solvents used were d^6-dimethylsulphoxide (DMSO) and deuterium oxide (D_2O), and the spectra extended from 0–14 ppm using tetramethylsilane (TMS) as an internal standard.

The mass spectra were carried out using Q1000–EXGC-MS Shimadzu spectrometer at 70 eV and MA energy, using a direct insertion probe at temperature 90–100°C.

RESULTS AND DISCUSSION

The elemental analyses of the chromone azo dyes for C, H and N were carried out. The obtained results are in good agreement with the theoretical values of the proposed tentative formulae. The melting points are uncorrected; these compounds are characterized by sharp melting point. It is to be mentioned that azo dyes derived from chromone III decompose on heating. Azo dye derivatives (d) containing arsono group are characterized by high melting points (Table-1).

The IR spectra of the chromone azo dyes under investigation are recorded as KBr discs. The IR-band assignments of these spectra are listed in Table-2. The IR spectra show broad bands at 3685–3413 cm^{-1} for (Ia–d), 3577–3500 cm^{-1} for (IIa–d) and 3431–3400 cm^{-1} for (IIIa–d) assigned to ν_{OH}. It can be concluded that the hydroxyl group of the chromone azo dyes are involved in hydrogen bond formation.[13] The spectra of dyes Ic, IIc and IIIc display a broad band at 2623, 2614 and 2625 cm^{-1}, respectively, which may be due to the carboxylic group in these derivatives being invoked in hydrogen bonding.[14] The spectra of derivatives d display a multiple broad band at 3500–3400 cm^{-1} due to the presence of extra other hydroxylic groups of $AsO(OH)_2$ on phenyl ring.

TABLE-1
ELEMENTAL ANALYSES OF THE CHROMONE AZO DYES UNDER INVESTIGATION

Compound	m.p. (°C)	Analysis % Found (Calcd.)		
		C	H	N
Ia	172	64.00	3.70	7.60
		(63.90)	(4.14)	(8.28)
Ib	162	61.20	4.20	7.40
		(61.00)	(3.95)	(7.90)
Ic	198	59.80	4.20	7.00
		(59.68)	(3.66)	(7.33)
Id	290	46.70	4.00	5.70
		(46.76)	(3.24)	(6.06)
IIa	145	63.10	4.30	8.40
		(62.96)	(3.70)	(8.46)
IIb	155	60.40	4.00	8.00
		(60.00)	(3.53)	(8.23)
IIc	178	58.90	3.60	8.10
		(58.69)	(3.26)	(7.60)
IId	273	45.80	3.80	6.10
		45.54	(2.90)	(6.25)
IIIa	200 (dec.)	66.00	4.30	9.00
		(65.80)	(4.51)	(9.03)
IIIb	208 (dec.)	62.50	4.10	8.30
		(62.57)	(4.29)	(8.58)
IIIc	245 (dec.)	60.90	4.20	7.40
		(61.02)	(3.95)	(7.91)
IIId	250 (dec.)	47.10	3.50	6.10
		(47.00)	(3.45)	(6.45)

The IR bands arising from C—H stretching vibration appeared in aromatic compounds at 3100–3000 cm^{-1}, and may thus be differentiated from saturated compounds.[14] The IR spectra of the chromone azo dyes under investigation show bands at 3164–3065 cm^{-1} corresponding to C—H stretching of aromatic ring.

The bands due to C—H stretching vibrations of alkanes are found in the range 3000–2850 cm^{-1}. Two strong bands appear at 2960 ± 10 and 2872 ± 10 cm^{-1} in hydrocarbons containing methyl group.[14] The absorption bands observed in the IR spectra of all azo dyes in the range 3082–2925 cm^{-1} can be assigned to the C—H stretching vibration of methyl group in position two. The intensity of this band is markedly increased due to the presence of methyl group in position six

TABLE-2

IR-BANDS (cm^{-1}) ASSIGNMENT OF CHROMONE AZO DYES

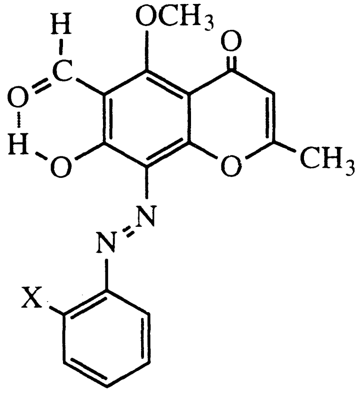
Ia	Ib	Ic	Id	IIa	IIb	IIc	IId	IIIa	IIIb	IIIc	IIId	Band assignment
3481	3420	3685–2623	3413	3577	3577	3577–2614	3500	3421	3418	3431–2625	3400	ν(OH)
3066	3076	3072	3082	3067	3071	3071	3070	3065	3069	3164	3070	ν(C—H) (Arom)
2963	2963	2951	—	2962	2962	2930	2930	2925	2927	2928	2930	ν(C—H) (CH_3)
—	—	1702	—	—	—	1662	—	—	—	1630	—	ν(C=O) (COOH)
1672	1672	1686	1671	1662	1662	1654	1680	1658	1657	1651	1658	ν(C=O) (chromone)
1638	1638	1647	1671	1647	1636	1647	1650	—	—	—	—	ν(C=O) (CHO)
1586	1586	1584	1587	1584	1582	1580	1585	1588	1618	1589	1620	ν(C=C)
1432	1433	1438	1434	1432	1432	1436	1440	1419	1426	1409	1415	ν(N=N)
1260	1260	1345	1263	1292	1292	1346	1290	1299	1298	1256	1290	ν(C—O)
1114	1114	1117	1114	1114	1114	1115	1115	1120	1141	1157	1130	δ(OH)
1086	1042	1086	1086	1042	1032	1045	1040	1032	1035	1040	1040	ν(C—O) Sym
853	866	878	863	853	853	848	853	847	849	852	840	ν(C—H) (deformation)
760	758	710	713	759	755	761	770	765	753	758	750	ν(C—H) (bending)

in derivatives (IIIa–d). The C—H stretching bands of methoxyl groups are found in the range 2832–2815 cm^{-1}.[15] The stretching vibration band of methoxyl group in position five in the chromone azo dyes (Ia–d) was undistinguished due to the presence of —CH_3 and OH groups.

TABLE-3
PROTON NMR SPECTRAL DATA OF THE CHROMONE AZO DYES

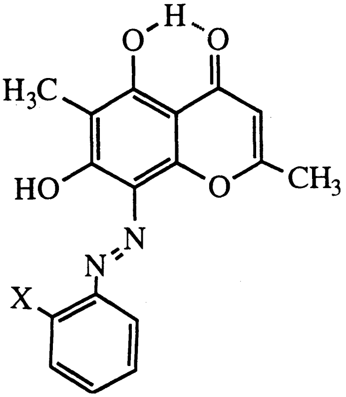
Series	a	b	c	d	assignment
I	2.3	2.3	2.3	2.3	CH3
	6.1	6.1	6.1	6.1	C–3
	12.0	12.0	11.8	—	OH
	7.4–8.2	7.4—8.2	7.4–8.2	7.4–8.2	Arom.protons
	10.2	10.3	10.3	10.2	CHO
	—	—	12.4	—	COOH
II	2.3	2.3	—	2.3	CH3
	6.1	6.1	—	6.2	C–3
	11.9	11.7	—	—	OH
	7.4–8.2	7.4–8.2	—	7.4–8.2	Arom.protons
	10.2	10.3	—	10.2	CHO
	—	—	13.0	—	COOH
III	2.3	2.2	2.2	2.2	CH3
	6.3	6.2	6.4	6.3	C–3
	11.3	11.7	11.7	—	OH
	7.2–8.0	7.2–8.0	7.2–8.0	7.6–8.2	Arom.protons
	—	—	11.7	—	COOH

El-Roudi[13] studied the IR spectra of the hydroxychromones containing formyl group. He found two absorption bands at 1675 and 1650 cm^{-1} due to the C═O stretching of the chromone moiety and formyl group, respectively. The IR spectra of the chromone azo dyes (Ia–d) under investigation display two strong bands in the range 1686–1671 cm^{-1} and 1647–1638 cm^{-1} corresponding to the C═O stretching of the chromone moiety and formyl carbonyl, respectively. The shift of the formyl carbonyl band to lower wavenumber in the derivatives Ia–c may be due to the presence of intramolecular hydrogen bond between C═O group of formyl group in position six and the OH group in position seven.



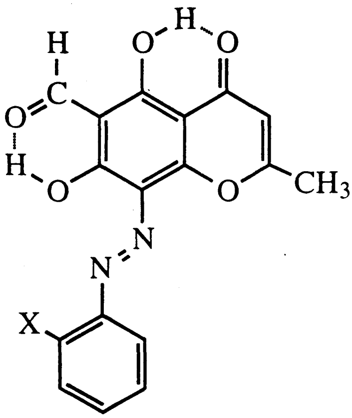
It is noticed that for the dye Id, the formyl carbonyl band interferes with the chromone carbonyl and appears as single band at 1671 cm^{-1}. This may be attributed to the mesomeric effect of the arsono group in the *ortho* position to the azo group.

Azo dyes belonging to series III (IIIa–d) exhibit one strong band at 1658–1651 cm^{-1} assigned to the chromone carbonyl. The shift of this band to lower wave-number may be due to the formation of a strong intramolecular hydrogen band between C═O group of the chromone moiety and the —OH group in position five, thus:



Also, the replacement of the formyl group by the CH_3 group will be in favour of such strong hydrogen bond formation.

The IR spectra of the azo dyes (IIa–d) under investigation display two strong bands at 1680–1654 cm^{-1} and 1650–1636 cm^{-1} due to the chromone carbonyl in position four and formyl group in position six, respectively. The shift of these bands to lower wavenumber is expected to be intramolecularly hydrogen bonded with the —OH groups in positions five and seven, respectively. Thus the structure of these dyes may be represented as follows:



It is to be mentioned that in the spectra of azo dyes Ic, IIc and IIIc, an extra band is observed at 1702, 1662 and 1630 cm^{-1} respectively ascribed to C═O stretching of the carboxylic group present in *ortho* position to the azo moiety.

The absorption bands appearing in the IR spectra of azo dyes at 1620–1580 and 1440–1409 cm^{-1} are due to ν(C═C) and ν(N═N) respectively. The bands at 1346–1256, 1157–1114 and 1086–1032 cm^{-1} are assigned to ν(C—O) stretching vibration, δ(OH) in-plane deformation and ν(C—O) symmetric vibration, respectively. While the weak bands of δ(CH) and γ(CH) appear at 878–848 cm^{-1} and 765–713 cm^{-1}, respectively.

The ^1H NMR spectra of chromone azo dyes (Ia–d and IIa–d) under investigation exhibit a singlet at 2.2–2.3 ppm with integration value equivalent to 3 protons, which is assigned to the CH_3 protons in the chromone moiety in position two, while in the case of the chromone azo dyes (IIIa–d), this signal appears at the same position and corresponding to the integration value of 6 protons which is attributed to the CH_3 protons in positions two and six in the chromone moiety. The presence of a methyl substituent at C–2 has marked effect on the shape of the signals from C–3 proton (proton of the pyrone ring) which is shortened and broadened in most cases and has been doubled in case of IId, IIIa, IIIb and IIIc. This effect is attributed to long range coupling with the C–2 methyl group.[16] The signal due to C–3 proton in the derivatives under investigation appears at 6.1–6.4 ppm. The signals observed at 7.2–8.4 ppm are attributed to the aromatic protons. The integration value in case of Ia, IIa and IIIa is five, while the integration value of other azo dyes is four. The spectra of azo dyes (Ia–d) and (IIa–d) exhibit a singlet at 10.2–10.3 ppm which is assigned to the aldehydic proton (integration value = 1). The signal observed at 12.4, 13 and 11.7 ppm in the spectra of compounds Ic, IIc and IIIc, respectively, is attributed to the proton of COOH group on the phenyl ring. The OH signal of the chromone moiety for Ia, Ib, IIa, IIb, IIIa, IIb and IIIc appears at 11.3–12 ppm due to its contribution in hydrogen bond formation which is in agreement with the results obtained from the IR study. The integration values of these signals correspond to one proton in case of Ia, two protons for (Ib, IIa and IIIa) and three protons for (IIb and IIIb). The arsonic OH signals and the chromone OH signals for Id, IId and IIId are not detected because they are present in the region of the signal of the solvent.

The interpretation of the mass spectrum requires an understanding of the fragmentation processes that occur before the ions reach the detector. Mass spectroscopy has proved extremely valuable for the determination of accurate molecular mass. It was stated that chromones exhibit a signal corresponding to molecular ions, and the loss of a neutral molecule of carbon monoxide (CO) is a very important fragmentation process.[17] It is observed that derivatives IIb, IIIa and IIIb exhibit molecular ion peaks at m/e equal 340, 310 and 326, respectively. This indicates the stability of their molecular ions. The most abundant fragment of IIIa and IIIb appears at m/e 205. The retro-Diels Alder reaction is observed in Ia, IIc, IIIa and IIIb by loss of neutral acetylene and charge retention on the fragment.

It is observed that the fragmentation patterns of the compounds Id, IId and IIId are difficult to interpret. This can be attributed to the presence of the arsone group which may undergo rearrangement to give fragmentation patterns not anticipated from the structure of the comopunds. However, the rest of the prepared azo dyes do not exhibit the signals of the molecular ion, which may be taken as evidence for its high instability.

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