

## Spectral Studies on Some Hydrazones of 6-Formyl-7-hydroxy-5-methoxy-2-methylchromone

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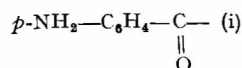
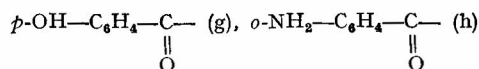
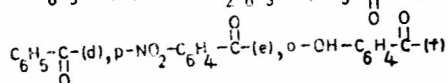
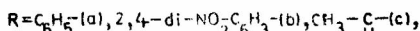
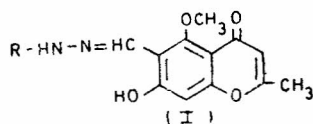
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The electronic absorption spectra of some hydrazones of 6-formyl-7-hydroxy-5-methoxy-2-methylchromone are studied in pure organic solvents of varying polarities and in aqueous medium at different pH values. The spectral changes are explained in terms of medium effect and molecular structure. The spectral shifts in buffer solutions are explained on the basis of an equilibrium set between molecular and ionic species existing in solution. The dissociation constants of the hydroxyl group for some compounds are determined from variation of absorbance with pH. The important bands in the IR spectra of the compounds are assigned and discussed in relation to molecular structure.

**S**PECTROPHOTOMETRIC studies of the hydroxyl derivatives of chromone are of interest since these compounds function as chelating agents, which are used as analytical reagents for the detection and determination of a large number of transition metal ions<sup>1,2</sup>. The electronic absorption spectra of chromone derivatives have also been investigated<sup>3-5</sup>.

The present investigation deals with the study of the electronic absorption spectra of some hydrazones (I) of 6-formyl-7-hydroxy-5-methoxy-2-methylchromone in organic solvents of varying polarities. The dissociation constants of some of these compounds have been determined spectrophotometrically in buffer solutions of varying pH.



### Materials and Methods

The compounds (Ia-i) were obtained by the condensation of the different acid hydrazides<sup>6</sup> with 6-formyl-7-hydroxy-5-methoxy-2-methylchromone, which was obtained by oxidation of visnagine with potassium dichromate<sup>7</sup>. The products were purified by crystallization from the appropriate solvent.

The solutions for measurements were obtained by diluting 10<sup>-3</sup>M stock solutions in the appropriate solvents (LR), purified by recommended

methods<sup>8</sup>; the buffer solutions were prepared as given by Britton<sup>9</sup>.

The electronic absorption spectra were recorded on a Unicam SP 900 spectrophotometer while the infrared spectra were obtained as KBr discs on a Unicam SP 200 infrared spectrophotometer.

### Results and Discussion

*Electronic absorption spectra in different solvents* — The electronic spectra of the compounds under investigation gave five absorption bands (Table 1). The first band is only observed in the spectra of some compounds in ethanol and ether. This band can be assigned to the  $\pi \rightarrow \pi^*$  transition within the aromatic rings corresponding to the (<sup>1</sup>L<sub>a</sub> → A) state. The second band, in analogy with many aromatic carbonyl compounds containing carbonyl group in a cyclic structure<sup>10</sup>, can be assigned to the  $\pi \rightarrow \pi^*$  of the aromatic ring (<sup>1</sup>L<sub>b</sub> → A) overlapping that of the  $\pi \rightarrow \pi^*$  transition involving the ring-carbonyl group ( $\phi \rightarrow C=O$ ) interaction.

The third and fourth bands are not observed in the spectra of Ia and Ib, i.e. in those compounds in which the hydrazone moiety is deprived of C=O group. Thus it seems that these bands are characteristic of the aroyl hydrazone structure<sup>11</sup>. The absence of the fourth band in the spectra of Ic and Id is in accordance with previous observations that substitution at the aromatic ring causes the appearance of the double band which is not the case of non-substituted systems. The bands on the visible side, not characteristic of locally excited transitions of the hydrazone or chromone systems, must be assigned to an intramolecular charge transfer (CT) interaction.

The position and extinction of the different absorption bands are influenced by the nature and order of substituents on the hydrazone moiety. The CT band is blue shifted as the donor character of the substituent increases. Thus the CT band in Ib is shifted towards red compared to Ia, indicating that the introduction of NO<sub>2</sub> group seems to

TABLE 1 — ELECTRONIC SPECTRAL BANDS OF VARIOUS COMPOUNDS IN DIFFERENT SOLVENTS

Solvent	[ $\lambda_{\max}$ (nm); $\epsilon_{\max}$ (litre mol <sup>-1</sup> cm <sup>-1</sup> × 10 <sup>-4</sup> )]									
	1st band		2nd band		3rd band		4th band		5th band	
	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$
COMPOUND Ia										
A	254	1.8	288	1.01					366	1.80
B	248	2.7	272	1.34					354	0.95
C	260	1.48	290	1.00					356	0.60
D	—	—	277	0.75					360	1.25
E	—	—	268	1.13					350	0.23
COMPOUND Ib										
A			294	1.02					378	0.75
B			262	Sat.					346	Sat.
C			268	do					382	do
D			264	do					376	do
E			272	do					370	do
COMPOUND Ic										
A	231	2.51	285	4.10	338	1.10			374	0.75
B	230	0.81	265	1.56	336	0.51			368	0.25
C	—	—	273	2.00	336	0.50			370	0.13
D	—	—	272	3.75	336	1.53			367	0.75
E	—	—	272	4.25	338	0.50			370	0.12
COMPOUND Id										
A	236	1.65	296	2.12	345	0.55			380	0.91
B	234	1.32	264	1.50	345	1.68			374	0.82
C	—	—	272	1.54	343	1.21			372	0.13
D	—	—	270	3.50	343	1.72			370	0.15
E	—	—	272	4.46	342	0.50			370	0.25
COMPOUND Ie										
A			296]	2.35	—	—	—	—	390	0.65
B			278]	—	—	—	350	Sat.	370	Sat.
C			280	Sat.	350	Sat.	366	do	384	do
D			273	do	350	do	367	do	385	do
E			272	do	340	do	340	do	375	do
COMPOUND If										
A			292]	3.13	336	2.25	350	2.25	382	0.91
B			270]	—	—	—	—	—	—	—
C			294	Sat.	336	Sat.	350	Sat.	—	—
D			274	do	312	do	350	do	—	—
E			272	do	334	do	348	do	—	—
COMPOUND Ig										
A			298]	2.4	—	—	—	—	380	0.70
B			270]	—	336	Sat.	362	Sat.	370	Sat.
C			280	Sat.	349	do	365	do	383	do
D			271	do	348	do	366	do	386	do
E			271	do	342	do	364	do	—	—
COMPOUND Ih										
A			296	1.42	336	0.20	—	—	388	0.65
B			—	—	336	Sat.	356	Sat.	—	—
C			276	Sat.	348	do	366	do	382	Sat.
D			272	do	352	do	364	do	382	do
E			270	do	336	do	356	do	—	—
COMPOUND Ii										
A			284	1.85	—	—	361	1.32	402	(sh)
B			—	—	—	—	—	—	—	—
C			281	Sat.	350	Sat.	366	Sat.	384	Sat.
D			272	do	350	do	367	do	384	do
E			270	do	320	do	365	do	—	—

A=ethanol; B=ether; C=CHCl<sub>3</sub>; D=CCl<sub>4</sub>; and E=cyclohexane.

further the intramolecular charge transfer. Accordingly, it can be concluded that the intramolecular CT takes place from the hydroxychromone to the hydrazone moiety.

Comparing Ia with Ic, it is apparent that the CT band is red-shifted in Ic due to the high acceptor character of the hydrazone part in this compound. This behaviour is further supported by the red shift of the band from Ic to Id on replacing the CH<sub>3</sub> by the phenyl group. Also donor substituents on the aromatic ring in the *p*-position either slightly affect or do not influence the band position whereas acceptor substituents cause an apparent red shift compared to the non-substituted compound.

The bands corresponding to electronic transition within the hydrazone moiety show the general behaviour for these bands<sup>11</sup>. The bands shift to red on replacing the CH<sub>3</sub> group in Ic by phenyl ring in Id due to the increase of electron mobility and conjugation in the latter compound. The bands display the general shift to red with donor substituents and blue shift with acceptor ones. The *o*-substituted compounds display the bands at higher energy due to the blocking of the lone pair of electrons on the carbonyl group. The CT band is red-shifted in *o*-substituted compounds relative to the *p*-substituted ones especially when the substituent contains an active proton which is capable of forming an intramolecular hydrogen bond. This behaviour indicates an easier intramolecular hydrogen bond formation which denotes an easier intramolecular charge transfer in *o*-substituted compounds involving intramolecular hydrogen bonding due to increased planarity between the different parts of the molecules.

Both  $\lambda_{\max}$  and  $\epsilon_{\max}$  of the absorption bands seem to be readily influenced by the nature of the solvent used. Though most of the absorption bands are influenced by changing the solvent, yet the obvious effects are observed with the bands located above 300 nm. The bands below 300 nm assigned to  $\pi \rightarrow \pi^*$  transition of the benzenoid system are slightly red-shifted on increasing the polarity of the medium. This behaviour is in accordance with the  $\pi \rightarrow \pi^*$  nature of the electronic transition leading to these absorption bands.

The bands lying above 300 nm show the general shift to red with increasing solvent polarity. However, the shift is not very regular with all the compounds and the order of shift depends on the nature of the substituent on the aromatic ring.

The application of the Gati and Szalay<sup>12</sup> equation revealed that the shift in band position is not essentially due to changes of the dielectric constant of the medium. Also the dielectric functions given by Suppan<sup>13</sup> are not valid supporting that the role played by the dielectric constant of the medium is not the main factor responsible for the red shift observed. The shift of the bands would thus be due to combined effect of several factors essentially the dielectric properties of the solvent and the specific solute-solvent interaction. This latter type of interaction involves the solvation of the ground and excited states and the changes of the solvation energy during the electronic transitions as well as solute-solvent hydrogen bonding.

The CT band shows an obvious shift in ethanol compared to solvents of low polarity. The apparent red shift of the CT band in polar solvent is in the same direction on going from the non-ionic to the ionic form. This reveals that the CT is at least partially determined by the charge density on the oxygen of the hydroxyl group, a phenomenon which can be explained by an interaction of the hydroxyl group with the polar solvent molecules, acting as a proton acceptor. This interaction leaves a residual negative charge on the oxygen atom of hydroxyl group. Accordingly the intramolecular CT is enhanced leading to the red shift of the CT band in proton acceptor solvents.

In solvents of low polarity not capable of forming intermolecular hydrogen bonding the solute molecules exist essentially in the non-polarized state.

*Determination of dissociation constants* — The spectra of the compounds in aqueous media show regular changes with *pH* of the medium, especially the CT band. The absorbance of the CT band decreases with increase in *pH*; meanwhile a new band develops at a longer wavelength. The spectra show a clear isosbestic point denoting existence of an equilibrium between the non-charged molecules and ionized species. The plot of absorbance as a function of *pH* gives typical dissociation or association curve. These results are utilized for the determination of  $p_a^K$  of the compounds applying three methods given previously: (i) the half-height method<sup>14</sup>; (ii) the modified limiting absorbance method<sup>15</sup> since the *A-pH* curves exhibit a rather high background; and (iii) the Colleter method<sup>16</sup> as modified for acid-base equilibria<sup>17</sup>. The  $p_a^K$  values obtained (Table 2) indicate that the ionization constant is but slightly influenced by the nature of the hydrazone moiety. This reveals a slight interaction between the hydroxyl group and this part of the molecule in the compounds studied in buffer solutions (Ia-d).

*Infrared spectra* — A satisfactory assignment for the bands in Ia-i can be attained by comparing them with those of the parent 2-methylchromone<sup>18</sup> and the various hydrazides.

The  $\nu$ -OH appears as a strong broad band  $\sim 3500$  cm<sup>-1</sup>, indicating the existence of an intramolecular hydrogen bond, between the 7-OH and  $-C=N$  group. This is supported by the low frequency of the  $-C=N$  band. The existence of the  $-C=N$  band (within the 1640-1650 cm<sup>-1</sup> range) and  $\nu$ C-OH band at 1335-45 cm<sup>-1</sup>.

The bands at 1670 cm<sup>-1</sup> due to the  $-C=O$  group in the chromone moiety<sup>19</sup> is not shifted. This indicates that the various resonance forms of the chromone moiety<sup>3</sup> are not affected by variously substituted hydrazone moiety.

A band in the range 1680-1710 cm<sup>-1</sup> in all the compounds except Ia and Ib is assigned to the amide-I band. The existence of this band indicates that the compounds exist essentially in the keto-form. This band is shifted to lower frequency region in If and Ih as compared to Id, revealing a stronger intramolecular hydrogen bond between the carbonyl group of hydrazide and *ortho* hydroxyl group in compound If or *ortho* amino group in compound Ih.

TABLE 2 — DISSOCIATION CONSTANTS OF THE COMPOUNDS

(Results obtained in aqueous solutions)

Com- pound	CT band				<i>pKa</i> *		
	Non-ionic		Ionic		(i)	(ii)	(iii)
	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$			
Ia	365	5.7	380	4.8	10.40	10.60	10.52
Ib	388	4.4	422	8.9	10.50	10.48	10.50
Ic	310	2.8	364	3.4	10.70	10.66	10.67
Id	344	2.5	374	1.9	10.90	10.80	10.93

\*Obtained by three different methods: (i) half-height method<sup>14</sup>; (ii) limiting absorbance method<sup>15</sup>; and (iii) Colleter method<sup>16</sup>.

In the lower frequency range, the bands characteristic for the substitution of the aromatic ring vary in position and number<sup>20</sup> from one compound to another.

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