

EFFECT OF CHELATION ON THE INFRARED CARBONYL FREQUENCY OF HYDROXY-XANTHONES, BENZOPHENONES AND ANTHRAQUINONES

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ABSTRACT

The effect of chelation on the carbonyl frequency of xanthenes is to lower it just as in the case of flavanones, isoflavanones and simpler ketones. This supports the explanation given earlier regarding the special behaviour of flavones and isoflavones. Benzophenones and anthraquinones resemble xanthenes in this respect.

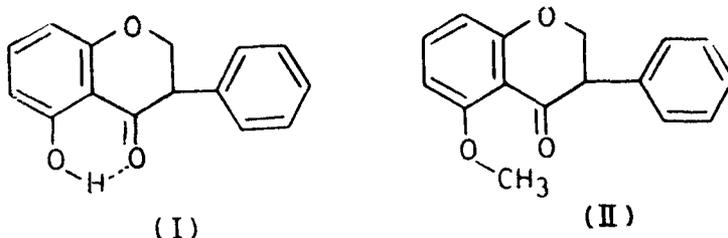
INTRODUCTION

In some of our earlier publications on the effect of conjugation and hydrogen bonding on the infrared (Raman) carbonyl frequency, certain abnormal features were noted. One of these related to the behaviour of 5-hydroxy flavonoids.¹⁻² A rational explanation for the abnormality has been provided in the most recent paper of the series.³

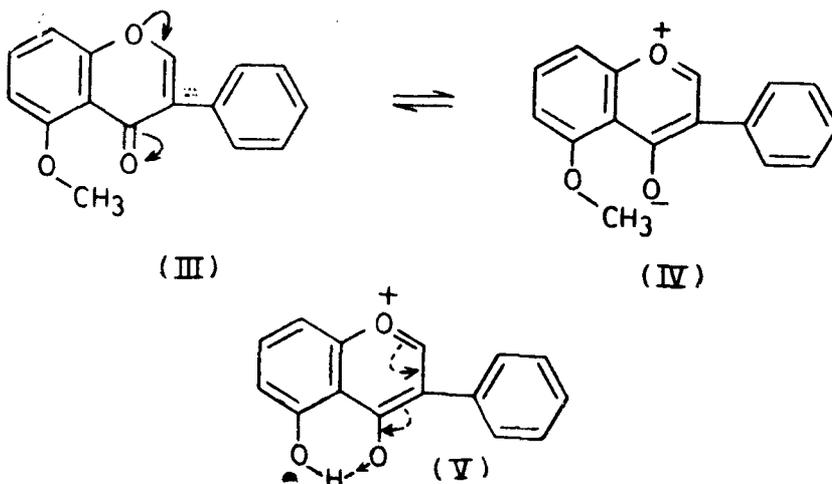
It was observed that the normal carbonyl frequency of isoflavanones and flavanones is decreased when a hydroxyl group is present in the 5-position.² For example in 5-hydroxy isoflavanone (I) the carbonyl group has a markedly lower frequency as compared to the 5-methoxy isoflavanone (II) attributable to the presence of intramolecular hydrogen bonding (chelation) between the 5-OH and the carbonyl group in the former and its absence in the latter. Comparison of analogous flavanones provides similar data and confirms the conclusion. This behaviour falls in line with those of simple carbonyl compounds such as esters, ketones and aldehydes.⁴⁻⁷

The situation is different with flavones and isoflavones in which a double bond is present in the pyrone ring. For example 5-hydroxy isoflavone has a carbonyl absorption at 1660 cm^{-1} whereas its methyl ether absorbs at 1640 cm^{-1} . In the former case the 5-hydroxy group is chelated to the carbonyl group and when this chelation is removed by methylation, as in 5-methoxy

isoflavone, the >C=O frequency instead of increasing is decreased. In an explanation offered² for this abnormal feature, the emphasis was laid on the predominant resonance structure (IV) in isoflavone tending to change to (V) when a 5-OH group is present. The initial situation of a flavonoid



skeleton with or without 5-methoxy group could be accommodated in the representations (III)-(IV). The carbonyl frequency is considerably reduced (1640 cm^{-1}) because of the resonance between these two forms. The introduction of a 5-hydroxyl resulting in chelation disturbs this and tends to produce structure (V) which leads to the strengthening of the carbonyl bond. The same explanation holds good for the flavone derivatives also.



Xanthenes

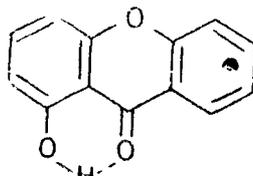
The main difference between the flavones and isoflavones on the one hand, and flavanones and isoflavanones on the other, is the presence, in the former, of the ethylenic double bond in the pyrone ring and this seems to establish effective conjugation of the ring oxygen with the carbonyl group. Though in the latter group (flavanones and isoflavanones) also there is a benzene double

bond capable of bringing about the same conjugation, it does not seem to be effective probably due to the reason that it is involved in a resonating benzenoid system with diminished double bond character. If this is so, the point could be checked by the study of xanthenes in which there are two benzene rings on either side of the γ -pyrone. The results of the study of the infrared spectra of a select series of suitably substituted xanthenes are presented in Table I. It will be clear from the data that the above explanation is valid since the effect of hydroxy groups producing chelation and its removal either by methylation of hydroxy group or by their acetylation or by their total absence, is very similar to those found in flavanones and isoflavanones.

TABLE I

Xanthone	ν_{CO} in cm^{-1}
1. Xanthone	1655
2. 1-Hydroxy-	1642
3. 1-Acetoxy-	1655
4. 1-Methoxy-	1650
5. 1, 8-Dihydroxy-	1635
6. 1, 8-Diacetoxy-	1656

Simple unsubstituted xanthone has carbonyl absorption at 1655 cm^{-1} . When a hydroxyl group is introduced in position 1 (or 8), the carbonyl frequency is lowered to 1642 cm^{-1} due to chelation (VI). When this effect is removed by esterification or etherification, the carbonyl frequency rises up to that of the unsubstituted xanthone (1655 cm^{-1}).



(VI)

Intramolecular hydrogen bonding (chelation) in 1-hydroxy xanthone is supported by a broad hydroxyl band at 3500 cm^{-1} and by the fact that the

-OH stretching frequency does not change markedly on dilution when the spectrum is taken in CCl_4 . Further support is provided by the fact that 1-hydroxy xanthone melts at much lower temperature (m.p. $148-49^\circ$) than 1-acetoxy xanthone (m.p. $170-71^\circ$) and 3-hydroxy xanthone (m.p. 240°).

It is known that xanthenes are structurally and biogenetically closely related to benzophenones. A series which could indicate the gradation in the I.R. frequency of the carbonyl group would be acetone, acetophenone, benzophenone and xanthone (*see* Table II). Stepwise increase of the benzene

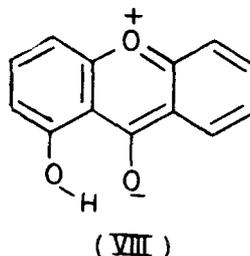
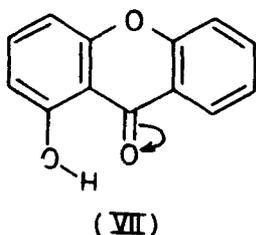
TABLE II^{8, 10}

Compound	$\nu\text{CO cm}^{-1}$
1. Acetone	1718
2. Acetophenone	1687
3. 2-Hydroxy-	1635
4. 2-Acetoxy-	1678
5. 2-Methoxy-	1649
6. Benzophenone	1665
7. 2-Hydroxy-	1648
8. 2-Methoxy-	1658

rings is accompanied by the gradual decrease in the infrared frequency of the carbonyl group. Flavanones and isoflavanones exhibit close resemblance to acetophenone whereas xanthenes resemble benzophenones. Thus acetone absorbs at 1718 cm^{-1} but when one methyl group is replaced by a phenyl group (thereby increasing conjugation or resonance stabilization), the carbonyl frequency is lowered to 1687 cm^{-1} . Further lowering of frequency is observed when the second methyl group of acetone is also replaced by a phenyl (benzophenone, 1665 cm^{-1}). When a hydroxyl is present in these derivatives at a position suitable for chelation, still more lowering in the carbonyl frequency is observed. However *o*-hydroxyacetophenones suffer more lowering as compared to the corresponding *o*-hydroxy benzophenones, obviously due

to the difference in the strength of the >C=O bond in the two cases, which is indicated by the difference in the infrared frequency; benzophenone has a lower >C=O frequency (1665 cm^{-1}) as compared to acetophenone (1687 cm^{-1}).

The interrelated study of aromatic ketones and xanthenes supports the view that the conjugation effect of the pyrone oxygen is relatively unimportant in xanthenes (VIII) which behave analogous to benzophenones in which there is no pyrone ring (VII). This confirms the earlier explanation about the infrared >C=O frequencies of flavones and isoflavones.

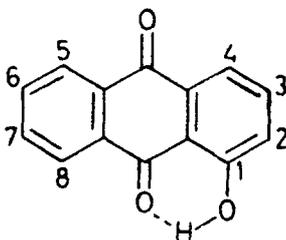


Insignificant Contribution
to the resonance hybrid
of xanthone.

Anthraquinones

Anthraquinones can also be considered to be somewhat similar to benzophenones in structure, the difference being that there are two carbonyl groups bridging the two benzene rings instead of one. The >C=O frequency of an unsubstituted anthraquinone is 1676 cm^{-1} . In 1-hydroxy anthraquinone, one of these two carbonyl groups has undergone chelation, resulting in the appearance of two carbonyl frequencies one lower (1636 cm^{-1}) corresponding to the chelated carbonyl (IX) and the other higher (1673 cm^{-1}) due to the unchelated carbonyl. The band corresponding to hydroxyl stretching is not observed in 1-hydroxy anthraquinone. This observation together with the shifting of the >C=O frequency to 1636 cm^{-1} indicates marked weakening of the OH and C=O bands, suggestive of very strong chelation.

In 1, 4 and 1, 5-dihydroxy anthraquinones both the carbonyl groups are involved in chelation and there is only one >C=O frequency in the infrared for each compound. It is 1627 cm^{-1} for 1, 4-dihydroxy and 1639 cm^{-1} for 1, 5-dihydroxy compound. Obviously the two chelated >C=O groups are equivalent in these compounds. The corresponding 1, 4 and 1, 5-dimethoxy anthraquinones tend to approximate to the unsubstituted anthraquinones and absorb at the normal >C=O frequency of anthraquinones (1670 cm^{-1}), though there is a small difference arising due to the electromeric effect of methoxy substituents.



(IX)

In the above discussion, we have kept ourselves to the study of the effect of chelation and its removal in xanthenes, benzophenones and anthraquinones. In the case of all these three groups the change in the IR spectrum by the presence of other substituents and their nature (electrophilic or nucleophilic) is normal just as in other benzene derivatives. Nucleophilic substituents, by virtue of their electromeric effect, tend to reduce the >C=O frequency and weaken the >C=O bond whereas the electrophilic substituents have the opposite effect. The position of these substituents with respect to the carbonyl group is also important. It is observed that the substituents in ortho and para positions convey the effect satisfactorily whereas the groups in the meta position do not. The effect of polar substituents is however small and does not interfere with the effect of chelation. Thus in 1,3 dihydroxy xanthone, the shift in the carbonyl frequency due to hydrogen bonding together with the electromeric effect is the same as in 1-hydroxy xanthone.

TABLE III

Compound	$\nu_{\text{CO}} \text{ cm}^{-1}$
1. 1, 3-Dihydroxy xanthone	1642
2. 1, 3-Diacetoxy-	1658
3. 3, 8-Dihydroxy-	1644
4. 3, 8-Diacetoxy-	1654
5. 1, 3, 7-Trihydroxy-	1625
6. 1, 3, 7-Triacetoxy-	1654
7. 1, 8-Dihydroxy-2, 6-dimethyl-	1638
8. 1, 3, 5, 8-Tetrahydroxy- ¹¹	1635
9. 1-Hydroxy-6-methoxy-3, 8-dimethyl-	1647
10. <i>p</i> -Amino benzophenone ¹⁰	1651
11. <i>p</i> -Bromo- ¹⁰	1665
12. <i>p</i> -Methoxy- ¹⁰	1658
13. <i>p, p</i> -Dimethoxy- ¹⁰	1655

EXPERIMENTAL

All the infrared spectra were recorded in KBr pellets. Column and thin-layer chromatography was done with silica gel G. The chromatograms (TLC plates) were viewed under UV light and if there was no fluorescence, the TLC plates were kept in I₂ jar for development. The solvent systems used for checking purity in TLC were (i) ethyl acetate, (ii) ethyl acetate : benzene (4 : 1), (iii) benzene : ethyl acetate : ethanol (50 : 43 : 7) for xanthenes and (iv) benzene : ethyl acetate (4 : 1), (v) chloroform : methanol (4 : 1), (vi) benzene : ethyl acetate : ethanol (72 : 25 : 3) for xanthone methyl ethers and acetates.

Preparation of Xanthenes and their Acetates and Methyl ethers

1-Hydroxy, 1, 8-dihydroxy and 1, 3, 7-trihydroxy xanthenes were prepared by employing Nencki's reaction, *i.e.*, treating the corresponding phenol

with appropriate *o*-hydroxy benzoic acid in the presence of fused zinc chloride¹² followed by extensive column and preparative thin layer chromatography. The rest of the xanthenes were prepared by Grover, Shah and Shah method¹³ using fused zinc chloride and POCl₃ as condensing reagent. All the compounds were recrystallised before taking the spectra. The acetates were prepared by Ac₂O- pyridine method and the methyl ethers, by refluxing the xanthone with dimethyl sulphate and anhydrous potassium carbonate in acetone solution. Completion of methylation was indicated by a negative ferric reaction. Purity of the samples was checked by TLC, employing the above-mentioned solvent systems.

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