

EFFECT OF CONJUGATION AND COMPLEX FORMATION ON THE RAMAN AND I.R. FREQUENCIES OF THE CARBONYL GROUP

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ABSTRACT

New data presented regarding the influence of different types of substituents in the benzene ring of aromatic carbonyl compounds (including benzils) on the $\nu_{\text{C=O}}$ frequency have made it possible to revise and rationalise older explanations.

Based on uniform considerations of polarisation, rational explanation can be provided for the effects of ethylene and phenyl conjugation, hydrogen bond formation and complex formation. Abnormal effects are observed in special cases where other important factors are simultaneously involved as for example in N-oxides and flavonoids of various types; but they are explicable on a rational basis. Further, the behaviour of acetylene and nitrile compounds throws insight on the nature of some of these factors.

EFFECT of conjugation and solvent (H-bonding) on the $\nu_{\text{C=O}}$ frequency of aldehydes, ketones and esters was studied earlier by Murty and Seshadri¹⁻⁴ using the Raman Effect. They noticed¹ that an ethylenic double bond conjugated to a $\nu_{\text{C=O}}$ group lowers its frequency and that the frequency of the ethylenic double bond also was lowered.

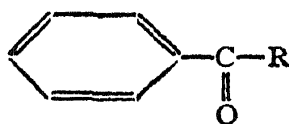
A similar effect of the phenyl group was also investigated by them² and they observed that the $\nu_{\text{C=O}}$ frequency is lowered when it is directly attached to the phenyl group as in benzoyl derivatives and enhanced when attached through oxygen atom as in phenyl esters.

With a view to studying the influence of the nature and position of the substituent in the phenyl ring on the $\nu_{\text{C=O}}$ frequency, infrared spectra of *o*, *m* and *p*-nitro and methoxy benzaldehydes, acetophenones and methylbenzoates have now been recorded. The I.R. spectra of some of these

carbonyl compounds mostly *p*-substituted had already been recorded⁵⁻¹⁰ either in nujol or concentrated solutions in CHCl_3 . To eliminate the solvent effect, the spectra have now been recorded in dilute solutions of CCl_4 . The >C=O frequencies of the substituted compounds together with those of the parent compounds are presented in Table I.

TABLE I

>C=O stretching frequencies in the infrared spectra of substituted aromatic aldehydes, ketones and esters in CCl_4



Subst.	Benzaldehyde R=H	Acetophenone R=CH ₃	Methyl benzoate R=OCH ₃
	cm. ⁻¹	cm. ⁻¹	cm. ⁻¹
<i>o</i> -OCH ₃	1689	1674	1733
<i>m</i> -OCH ₃	1703	1680	1730
<i>p</i> -OCH ₃	1697	1677	1721
..	1703	1683	1724
<i>p</i> -NO ₂	1709	1694	1727
<i>m</i> -NO ₂	1706	1691	1733
<i>o</i> -NO ₂	1712	..	1730

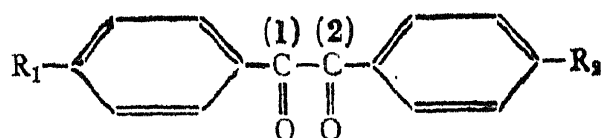
The earlier explanation of Murty and Seshadri² for the influence of phenyl ring on the >C=O frequency laid emphasis on resonance and it appeared that the influence of the phenyl group differed when it is linked straight to the >C=O group as found in esters of benzoic acid and phenyl ketones and when it is linked through oxygen as found in phenyl esters (VIII).

Their results and those obtained now require rational explanation based on a uniform consideration. This possibility has been emphasised by our recent work on Infrared spectra of benzils¹¹ where the presence of

methoxy and nitro substituents have been found to have opposite effects and the former really reduces the $\nu_{\text{C=O}}$ frequency. In these compounds the two carbonyls are independent and the effect of substitution on each of the benzene rings could be recorded on the attached carbonyl.

TABLE II

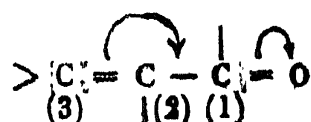
$\nu_{\text{C=O}}$ stretching frequencies of benzils in CHCl_3



R_1	R_2	$\nu_{\text{C=O}}$ frequency cm.^{-1}	
		$\nu_{\text{C=O}}$ (1)	$\nu_{\text{C=O}}$ (2)
H	$\text{N}(\text{CH}_3)_2$	1677	1661
H	OCH_3	1677	1671
OCH_3	OCH_3	..	1671
H	H	1677	..
H	Cl	1677	1689
H	NO_2	1677	1691
NO_2	NO_2	..	1691

The mechanism by which they affect the $\nu_{\text{C=O}}$ group should be the same in all the $\nu_{\text{C=O}}$ compounds already studied and this mechanism and its applications to different typical cases are discussed below:

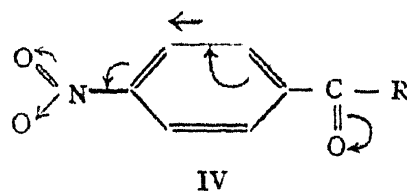
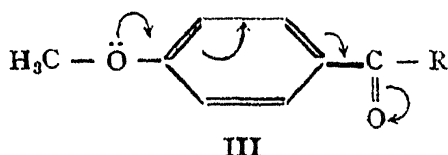
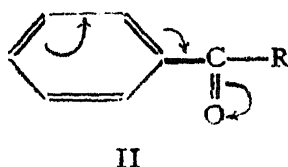
(1) *Ethylenic conjugation with $\nu_{\text{C=O}}$ group.*—The data recorded by Murty and Seshadri¹ indicate that ethylenic conjugation reduces the $\nu_{\text{C=O}}$ frequency as also that of the ethylenic double bond. It is generally known that in these conjugated systems the $\nu_{\text{C=C}}$ bond can polarise in either direction and the $\nu_{\text{C=O}}$ group controls the direction of polarisation. The polarised system can be represented as



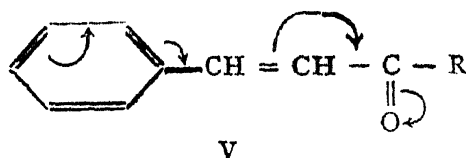
This will tend to reduce the >C=O frequency and also that of the >C=C< bond as observed. The single bond between (1) and (2) carbon atoms derives some double bond character.

(2) *Phenyl conjugation*.—The earlier observation of Murty and Seshadri² showed that in esters of benzoic acid, acetophenone, benzophenone, benzaldehyde and benzoyl chloride as compared with the corresponding non-benzenoid compounds, there is marked lowering of frequency. In the course of the present work (see Table I), it has been pointed out that the effect on the >C=O frequency of the substituents present in the benzene ring is again marked. In general, substitution in the *meta* position has small or negligible effect whereas that in *ortho* and *para* positions has considerable effect. It is also significant that an electron source like methoxyl tends to reduce the >C=O frequency and electron sink like NO_2 enhances it.

These observations can be uniformly explained on the basis that the phenyl ring behaves like the ethylenic linkage as an electron source as given in formula II and consequently encourages the polarisation of the >C=O group and reduces the >C=O frequency. In this function of the phenyl group, a methoxyl in the *ortho* or *para* position will add to its efficiency as electron source, and thus further reduces the >C=O frequency (III) whereas a nitro group as is well known has the opposite effect (IV).



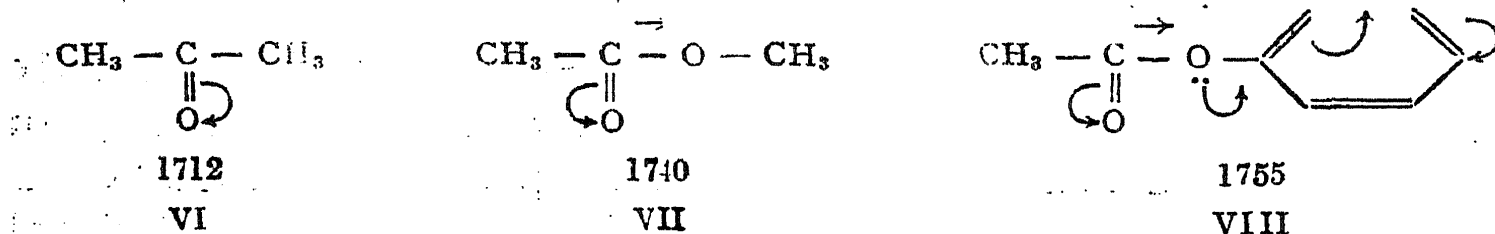
When the conjugation is extended from the benzene ring by an ethylenic bond as in cinnamic esters, aldehydes and ketones, the same effect is felt and the >C=O frequency falls in these cases also (V).



It is characteristic of the ethylenic link as well as the phenyl ring that they can act both as electron sinks and as electron sources and how they act in a particular situation is decided by the attached groups. Because of

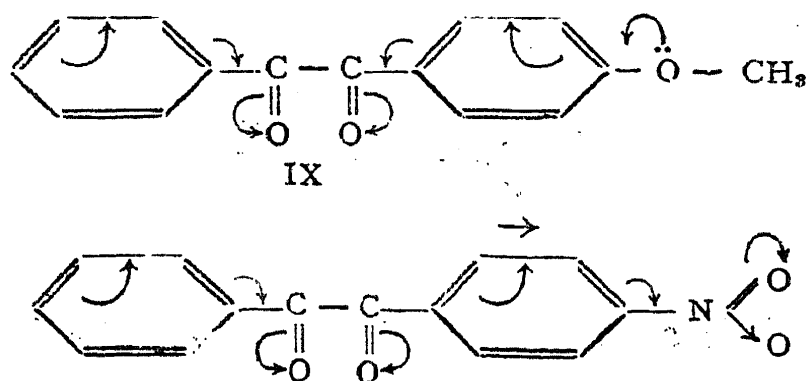
the marked effect of the >C=O group, the attached benzene ring acts always as an electron source. This is supported by chemical and physical properties of all compounds containing $\text{C}_6\text{H}_5\text{C=O}$ group. Owing to loss of electrons, the nuclear positions, particularly *ortho* and *para*, have reduced activity.

On the other hand, in discussing the behaviour of the phenyl group in phenyl esters in which the >C=O frequency is considerably enhanced, we have first to consider the behaviour of esters as compared to the related ketones. The esters have markedly higher >C=O frequency, e.g., methyl acetate (1740 cm.^{-1}) and acetone (1712 cm.^{-1}). In a reasonable explanation, this could be attributed to the general effect of the ester oxygen as electron attractant as shown in formula VII and this reduces the normal >C=O polarisation with the consequence that the >C=O frequency becomes higher.



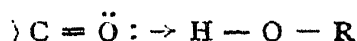
In phenyl acetate, the phenyl group is in a situation in which as in phenol and its ethers it acts as an electron sink. This is supported by the greater reactivity of nuclear positions. Consequently the >C=O polarisation will be further reduced and the frequency of the group further enhanced (1755 cm.^{-1}). This explanation is fully reasonable because in all situations where oxygen is linked to the phenyl, the reactivity of the phenyl is enhanced. When the electron withdrawing effect of the phenyl is further enhanced by NO_2 group as in nitro phenyl acetate the >C=O frequency should, according to these considerations, go still higher up. This is in fact so as recorded in I.R. by Freedman¹³ as 1779 cm.^{-1}

Reference may be made here to the study of vinyl acetate²³ in which the vinyl (ethylene) group produces the same effect as the phenyl in phenyl esters mentioned above.



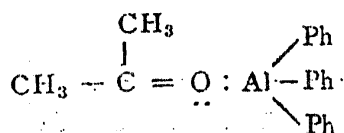
A similar explanation becomes valid for the observations on benzils¹¹ which are quite analogous to aromatic ketones (see Table II). As a consequence of the polarisation of the >C=O groups enhanced by the phenyl and more so by the anisyl, the >C=O bond becomes less of a double bond in character and hence the frequency is lowered (IX). Nitro group as an electron sink has an opposing effect and hinders this polarisation and increases the >C=O frequency (X).

Hydrogen bond formation.—In the earlier studies^{3,4} of the solvent effect on the >C=O frequency using the Raman Effect, solvents like CHCl_3 and $\text{C}_6\text{H}_5\text{OH}$ were found to lower the >C=O frequency and this is the general observation regarding such associations. The degree of lowering depends in general both on the nature (capacity) of the >C=O group as donor and nature (capacity) of the solvent as acceptor. But other factors have effect, especially when other groups are in conjugation with the >C=O .

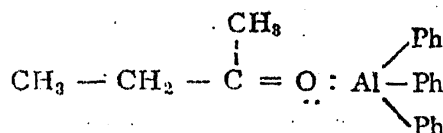


Carbonyl compounds are also known to form adducts or complexes^{21, 22} with BCl_3 , BF_3 , AlCl_3 , AlPh_3 , FeCl_3 and TiCl_4 . The spectra of the adducts reveal a marked lowering of >C=O frequency on oxygen-metal bond formation. This is evidently due to the effect of co-ordination with metal similar to that of hydrogen bond formation.

But in these cases, apart from the conjugative influences, the size and nature of the groups present in both parts of the associations seem to have marked influence: (1) the influence of the groups attached to >C=O is indicated by the examples given below:



$$\Delta \nu = 46 \text{ cm.}^{-1}$$

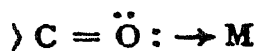


$$\Delta \nu = 61 \text{ cm.}^{-1}$$

(2) the effect of the nature of the acceptor groups is shown in Table III.

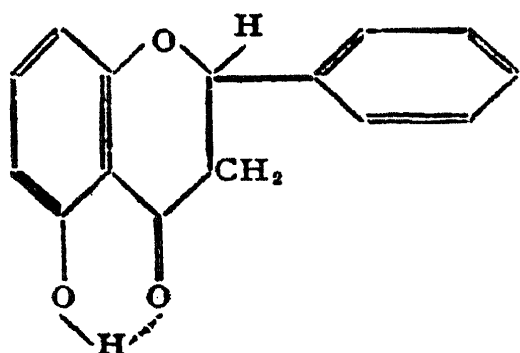
Abnormal effects are observed in special cases where other powerful factors are simultaneously involved. An important example of this type is the behaviour of 5-hydroxy flavonoids in which chelation between the OH group and the neighbouring >C=O is a marked feature. Isoflavanones of this type have been studied by the Infrared spectrum¹² and they behave normally in H-bonding, for example, 5-hydroxy isoflavanone and 5-OCH₃ isoflavanone. In the 5-hydroxy isoflavanone >C=O group has a markedly

TABLE III

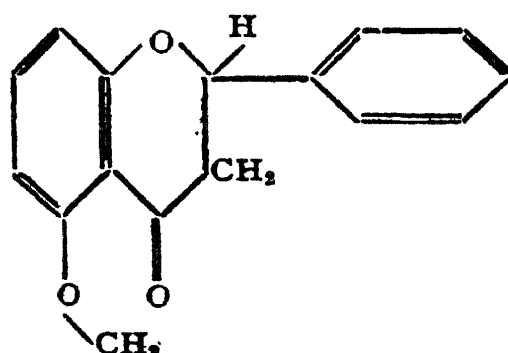
Shift in $\nu_{C=O}$ frequency on complex formation

Acceptor (M)	Donor		
	Benzophenone	Acetophenone	Acetone
	1657 cm. ⁻¹	1675 cm. ⁻¹	1710 cm. ⁻¹
HgCl ₂	..	18	..
ZnCl ₂	..	47	..
BF ₃	112	107	70
TiCl ₄	144	118	..
SnCl ₄	75
AlCl ₃	122	120	..
FeCl ₃	145	130	..
AlBr ₃	142	130	85

lower frequency as compared to methoxy compound. This may be attributed to chelation present in the former and its absence in the latter. Comparison of analogous flavanones provides similar data¹² and confirms the conclusion. This behaviour falls in line with those of simple $\nu_{C=O}$ compounds such as esters, ketones and aldehydes mentioned earlier.



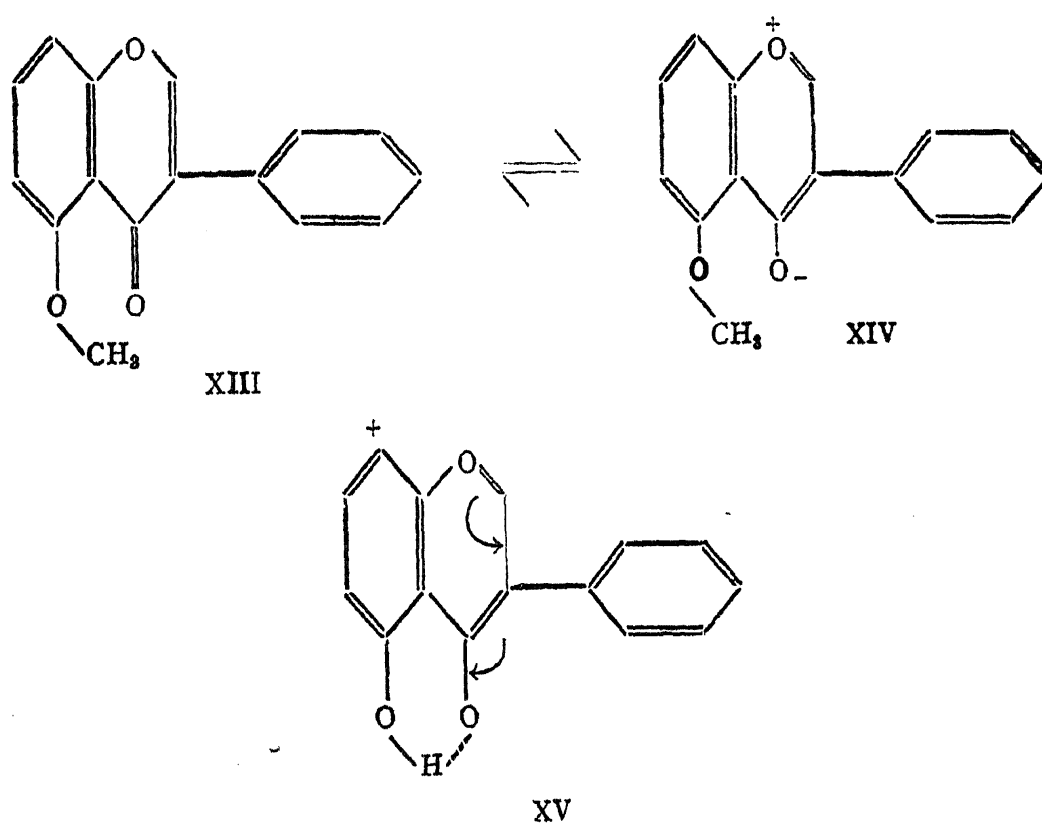
XI



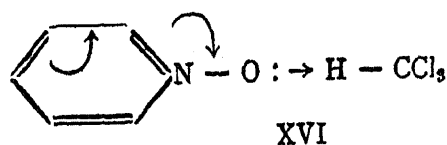
XII

The situation is somewhat different with flavones and isoflavones which have a double bond in the oxygen ring. For example, 5-hydroxy isoflavone

and its methyl ether have carbonyl frequencies at 1660 cm.^{-1} and 1640 cm.^{-1} respectively. In these cases, the effect of chelation is to increase the >C=O frequency. In the earlier explanation offered¹² for this feature the emphasis was on the predominant resonance structure XIV in isoflavone tending to change to XV when a 5-OH group is present. A small modification seems to be necessary. The initial situation of a flavonoid skeleton or the skeleton with 5-methoxyl could be accommodated in the representations XIII and XIV. The >C=O frequency is considerably reduced (1640 cm.^{-1}) because of this effect. The introduction of a 5-hydroxyl resulting in chelation disturbs this and tends to produce structure XV which leads to the strengthening of the >C=O bond as compared with the 5-methoxy compound.



It has been recently observed¹⁴ that with N-oxides of pyridine and quinoline, though the point of attack of the solvent is on the NO group, the N-O bond frequency markedly increases. This is due to the special structural features of these compounds and the strengthening of the bond could be explained as arising from the mechanism given below which results in the electromeric flow of electrons from the neighbouring double bond.



This capacity of N-oxide system of aromatic ring bases explains also its characteristic behaviour in substitution reactions.

A somewhat similar effect of H-bond formation has been brought to light by Thompson and White¹⁵ who recorded that in the association of nitriles with phenols for example acetonitrile, the $C\equiv N$ frequency is displaced to higher values. Similar observations had been made earlier¹⁶⁻²⁰ in regard to nitrile complexes with BCl_3 , $SnCl_4$ and $TiCl_4$ and also in regard to N-oxide formation in nitrile N-oxides the $C\equiv N$ frequency is higher than with nitriles.

These observations require special explanation: One way of viewing the situation will start with an understanding of the structure of $HC\equiv N$ and also of acetylene $H-C\equiv C-H$. In these two cases, the triple bond has a tendency to draw in more electrons thus leading to the ionisation of the proton. This leads to acetylene exhibiting weak acidic properties and HCN more prominently so. Thus there is a tendency to weaken the C—H bond and strengthen the C≡N bond. The same effect should exist in alkyl nitriles also. With the utilisation of nitrogen's lone pair electrons in complex formation and the formation of N-oxides mentioned above, the above-mentioned tendency for more electrons to flow into the C≡N bond seems to get accentuated and the bond strength increases. As support of the explanation may be mentioned, the observation of Thompson and White¹⁵ that with dichloro and trichloro acetonitrile, the $C\equiv N$ bond frequency does not increase on hydrogen bond formation, obviously due to the effect of the halogen atoms which have a tendency to withdraw the electrons towards them, thus creating an opposing effect.

Another way of looking at the matter will be by analysis of the orbitals involved. This has been done by Purcell and Drago¹⁶ in connection with complex formation of acetonitrile with BF_3 and $SnCl_4$. They consider that as a consequence of co-ordination the p -character of the original lone pair on nitrogen increases while the s -character of the $C\equiv N$ bond increases, thus causing shortening of the $C\equiv N$ bond and increase in its frequency.

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