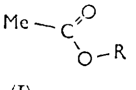
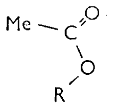
658. *Carbonyl Absorption in the Infrared Spectra of Phenolic Acetates*

By H. Lee and J. K. Wilmshurst

Infrared spectra in the 1600—1800 cm.$^{-1}$ region have been obtained for a number of hydroxy anthraquinone acetates, phenyl acetate, and α- and β-naphthol acetates. In solution or in the liquid phase, the acetate carbonyl absorption is found to consist of two overlapping bands arising as a result of Fermi resonance between a combination tone and the acetate carbonyl fundamental. Integrated intensities of the acetate and quinone carbonyl bands are reported for all the compounds studied.

In the course of a study of the vibrational spectra of simple esters, it was observed that the acetate derivatives of mono- and poly-hydric phenols exhibited a doubling of the acetate carbonyl band, the relative intensities of the pair of bands being dependent on both solvent and temperature. This behaviour is typical of that expected for conformational isomerism [1] and, since the acetates are capable of existing as two possible conformers [2] (I) and (II),


(I)


(II)

it was thought that these results warranted further investigation, especially as this would be the first instance of the observation of the *trans*-conformer (II) of an ester. However, interpretation of the observed values in terms of the coexistence of two conformers was found to present some difficulties, and we were accordingly led to conclude that the two carbonyl bands arise rather from the Fermi interaction of a combination tone with the acetate carbonyl fundamental.

Experimental

The acetates were prepared in the usual manner [3] and recrystallised three times from chloroform or chloroform–ethanol.

Infrared spectra were recorded on a Beckman IR-7 grating spectrometer. The spectra in the 1800 cm.$^{-1}$ region for liquid films, chloroform and carbon tetrachloride solutions of α- and β-naphthol acetates are shown in Figures 1a and b, respectively. Spectra of chloroform solutions of three anthraquinone acetates, also in the 1800 cm.$^{-1}$ region, are shown in Figure 1c, whilst the spectra of chloroform and carbon tetrachloride solutions of 2-hydroxy-anthraquinone acetate and phenyl acetate are shown in Figures 1d and e, respectively.

Integrated intensities of the acetate carbonyl band at ~1770 cm.$^{-1}$ and the anthraquinone carbonyl band at ~1680 cm.$^{-1}$ for chloroform and (where the solubility allowed) carbon tetrachloride solutions are given in Table 1 together with the band centres and molecular extinction coefficients of these bands. (The intensity recorded for the acetate carbonyl band is for the whole band. The positions and molecular extinction coefficients of the two components of this band were computed by least-squares fitting of two Lorentz-shaped curves to the observed band contour.)

Discussion

The observed behaviour of the acetate carbonyl band with respect to solvent and temperature (Figure 1) may be interpreted as arising from the coexistence of two conformers, or as due to Fermi resonance of a combination tone with the acetate carbonyl fundamental. For convenience we discuss these alternatives separately.

The Assumption of Conformational Isomerism.—In general, because of the effects of resonance, the skeleton of the carboxylate group in simple organic esters is planar [2] and, accordingly, two conformations *cis* (I) and *trans* (II), having different carbonyl frequencies,

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[1] S. Mizushima, " Structure of Molecules," Academic Press, New York, 1954.

[2] G. W. Wheland, " Resonance in Organic Chemistry," Wiley, New York, 1955, p. 235.

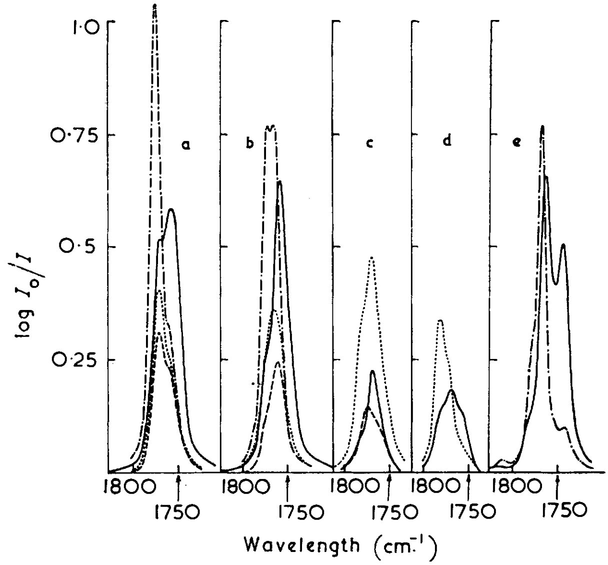
[3] A. I. Vogel, " Practical Organic Chemistry," Longmans, London, 1956, pp. 652, 669, 682.

are possible. In unsymmetrically substituted phenolic acetates, additional isomers, corresponding to the possibility of rotational isomerism about the aryl oxygen bond, may also occur, but these configurations should not affect the carbonyl frequency to any appreciable extent and we therefore ignore them here.*

Since the intensity of an infrared band is proportional to the number of molecules, n, times the intensity per molecule, k, the variation with temperature of the relative intensities of bands corresponding to different isomers may be used to determine the energy differences, ΔE, between the isomers by the equation

$$\log(I_0/I_1)/\log(I_0/I_2) = k_1n_1/k_2n_2 = (k_1/k_2)\exp(-\Delta E/RT).$$

For the α- and β-naphthol acetates, $\Delta E = 1{\cdot}54 \pm 0{\cdot}11$ and $1{\cdot}87 \pm 0{\cdot}05$ kcal. mole^{-1}, respectively, the higher-frequency carbonyl band corresponding to the least-stable isomer and having, in addition, the greater intrinsic intensity ($k_1/k_2 = 15$ and 5, respectively). The relative intensities of the two carbonyl bands in chloroform and carbon tetrachloride solution allow assignment of the higher-frequency band to the least-polar isomer. Calculation† indicates this to be the *cis*-isomer (I) and we therefore conclude the most stable conformer in these esters to be *trans*.



Infrared spectra of the acetate carbonyl band in the 1700—1800 cm.$^{-1}$ region

(a) α-Naphthol acetate: (— · — · —) CCl_4, (———) $CHCl_3$, (– – – –) liquid at 69°, (· · · ·) liquid at 132°; (b) β-naphthol acetate: (— · — · —) CCl_4, (———), $CHCl_3$, (– – – –) liquid at 65°, (· · · ·) liquid at 159°; (c) chloroform solutions of anthraquinone derivatives: (———) 1,5-dihydroxyanthraquinone diacetate (– – – –) 1-methoxy-2-methyl-3-hydroxyanthraquinone acetate, (· · · ·) 1,8-dihydroxyanthraquinone diacetate; (d) 2-hydroxyanthraquinone acetate: (· · · ·) CCl_4, (———) $CHCl_3$; (e) phenyl acetate: (— · — · —) CCl_4, (———) $CHCl_3$.

These results are surprising for four main reasons:

(*a*) the *trans*-isomer is the most stable, in contrast to the aliphatic esters where only the *cis*-isomer is observed; [4]

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* In phenyl acetate, rotation about the aryl oxygen band does not give rise to spectroscopically different isomers and hence, at least in this case, the observed complex carbonyl absorption certainly does not arise from this cause.

† Assuming bond moments $\mu_{Ph-O} = 0{\cdot}8$D, $\mu_{C-O} = 1{\cdot}1$D, and $\mu_{C=O} = 2{\cdot}7$D, the oxygen atom being the negative end of the dipole in each instance, we calculate $\mu_{cis} = 1{\cdot}67$D and $\mu_{trans} = 3{\cdot}16$D.

[4] J. M. O'Gorman, W. Shand, jun., and V. Schomaker, *J. Amer. Chem. Soc.*, 1950, **72**, 4222; S. Mizushima and M. Kubo, *Bull. Chem. Soc. Japan*, 1938, **13**, 174; R. J. B. Marsden and L. E. Sutton, *J.*, 1936, 1383; J. K. Wilmshurst, *J. Mol. Spectroscopy*, 1957, **1**, 201.

(*b*) the lower-frequency carbonyl band is associated with the *trans-* rather than the *cis-*isomer, contrary to the expectation that intramolecular hydrogen bonding in the latter would cause it to have the lower frequency;

(*c*) in the anthraquinone derivatives, the carbonyl frequencies of the two conformers are not particularly constant from derivative to derivative, the *trans*-conformer having the range 1761—1769 cm.$^{-1}$ and the *cis*-conformer the range 1771—1783 cm.$^{-1}$;

(*d*) in the naphthol acetates the integrated intensity of the whole acetate carbonyl band changes only relatively little from chloroform to carbon tetrachloride solution, although the relative population of conformers, having violently different intrinsic carbonyl intensities, changes markedly. Likewise, the constancy of the integrated intensity of the acetate carbonyl band in the different anthraquinone acetates, despite the obvious difference in the relative numbers of conformers present for each derivative, is an argument against interpretation of the acetate carbonyl doublet in these materials as arising from conformational isomerism. Thus, we must consider the alternative explanation.

The Assumption of Fermi Resonance.—If an overtone or combination tone belonging to the same symmetry species as a fundamental has a frequency near that of the fundamental, then the two bands may interact in such a way as to result in a symmetrical movement of both away from each other. In addition, the intensity of the combination tone is enhanced at the expense of the fundamental. If, in the absence of Fermi resonance, the combination tone can be assumed to have zero intensity, then the intensity of the combination tone borrowed from the fundamental by Fermi interaction can be written in terms of the observed intensity I_n of the perturbed fundamental together with the unperturbed frequencies of the combination tone ω_i^0, and fundamental ω_n^0, as

$$I_i = I_n(\delta - |\omega_n^0 - \omega_i^0|)/(\delta + |\omega_n^0 - \omega_i^0|)$$

where the observed (perturbed) frequencies are given by

$$\omega = \tfrac{1}{2}(\omega_n^0 + \omega_i^0) \pm \tfrac{1}{2}\delta$$

With the observed peak absorbances and frequencies, the unperturbed frequencies of the fundamental and overtone may be calculated from these equations, and the results for the derivatives studied in the present investigation are given in the Table. Four main points of agreement stand out:

(*a*) the unperturbed acetate carbonyl frequency is lower in chloroform than in carbon tetrachloride solution, as would be expected;

(*b*) the acetate carbonyl frequency in the anthraquinone acetates occurs at 1769 ± 1 cm.$^{-1}$ (in $CHCl_3$) except for the 1,8-, 1,2-, and 1,2,5,8-derivatives, which are a little higher;

(*c*) the intensity of the acetate carbonyl band in the anthraquinone derivatives is constant and depends only on the number of acetate groups in the molecule, as would be expected;

(*d*) as the temperature is increased by 65° and by 100° for the α- and β-naphthol acetates, the unperturbed carbonyl frequency increases 1·5 and 2·5 cm.$^{-1}$, respectively, which, although a little larger than may be expected, is nevertheless in the expected direction, corresponding to a lowering of the density of the liquid and a consequent decrease in intermolecular interaction.

Aromatic systems are characterised by a series of bands in the 1700—2000 cm.$^{-1}$ region due to summation tones of the C–H out-of-plane deformations,[5,6] the symmetry of these combination bands in the phenolic acetates being appropriate for Fermi interaction with the acetate carbonyl vibration.* In contrast, similar Fermi resonance of a combination

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* In phenyl acetate the combination tones observed are probably 836 + 903 and 836 + 934 corresponding to the combinations *g* + *i* and *g* + *h* of Whiffen.[6]

[5] C. W. Young, R. B. DuVall, and N. Wright, *Analyt. Chem.*, 1951, **23**, 709.

[6] D. H. Whiffen, *J.*, 1956, 1350.

Band positions, molecular extinction coefficients, and integrated absorption intensities for the acetate and quinone carbonyl bands

		Acetate carbonyl							Quinone carbonyl			Ratio acetate to quinone carbonyl intensities
		Observed				Calculated unperturbed frequencies		Integrated intensity [b]	cm.$^{-1}$		Integrated intensity [b]	
Derivative	Solvent	cm.$^{-1}$	ε [a]	cm.$^{-1}$	ε [a]	Fundamental	Combination		Asym C=O	Sym C=O		
Anthraquinones												
1-OAc	$\mathrm{CHCl_3}$	1771	0·68	1763	0·30	1769	1765	2·29	1677	~1674	2·71	0·844
2-OAc	$\mathrm{CHCl_3}$	1775	0·45	1761	0·41	1769	1768	2·16	1678	~1672	2·66	0·811
	$\mathrm{CCl_4}$	1782	0·71	1772	0·52	1777	1776	2·28	1679	~1676	2·72	0·838
1-OMe-2-Me-3-OAc	$\mathrm{CHCl_3}$	1783	0·11	1767	0·87	1769	1781	2·18	1676	~1673	2·80	0·777
1,2-$\mathrm{(OAc)_2}$	$\mathrm{CHCl_3}$	1782	1·34	1768	0·55	1778	1772	4·48	1678	~1674	2·82	1·590
	$\mathrm{CCl_4}$	1785	2·34	—	—	1785	—	4·82	1679	~1674	3·02	1·596
1,4-$\mathrm{(OAc)_2}$	$\mathrm{CHCl_3}$	1774	1·48	1763	0·86	1770	1767	4·60	1678	~1674	2·92	1·578
1,5-$\mathrm{(OAc)_2}$	$\mathrm{CHCl_3}$	1775	1·44	1762	0·85	1770	1767	4·57	1679	—	2·76	1·656
1,8-$\mathrm{(OAc)_2}$	$\mathrm{CHCl_3}$	1781	0·49	1768	1·29	1772	1777	4·42	1677	~1671	2·69	1·642
2,6-$\mathrm{(OAc)_2}$	$\mathrm{CHCl_3}$	1774	0·86	1766	0·97	1769	1770	4·55	1678	—	2·72	1·675
1,2,5,8-$\mathrm{(OAc)_4}$	$\mathrm{CHCl_3}$	1781	1·70	1769	1·84	1775	1775	8·68	1680	—	2·71	3·204
Naphthalenes												
1-OAc	$\mathrm{CHCl_3}$	1770	0·47	1755	0·63	1761	1763	2·48	—	—	—	—
	$\mathrm{CCl_4}$	1775	1·27	1758	0·23	1772	1761	2·58	—	—	—	—
2-OAc	$\mathrm{CHCl_3}$	1774	0·13	1757	0·89	1759	1772	2·41	—	—	—	—
	$\mathrm{CCl_4}$	1773	0·72	1763	0·77	1768	1768	2·31	—	—	—	—
Benzene												
OAc [c]	$\mathrm{CHCl_3}$	1764	0·71	1744	0·51	~1756	—	2·56				
	$\mathrm{CCl_4}$	1768	1·22	1741	0·12	~1768	—	2·44				

[a] $\varepsilon = \frac{1}{cl}\log_e (I_0/I)$ in units of 10^3 l. mole^{-1} cm.$^{-1}$. [b] Integrated intensity $= \frac{1}{cl}\int \log_e (I_0/I) d\omega$ in units of 10^4 l. mole^{-1} cm.$^{-2}$. [c] Also showed bands at 1783 cm.$^{-1}$ (ε 0·04) in $\mathrm{CHCl_3}$ and 1779 cm.$^{-1}$ (ε 0·22) in $\mathrm{CCl_4}$.

tone with the acetate carbonyl is not generally observed in the aliphatic acetates.[4,7] Thus, we conclude that the origin of the doubling of the acetate carbonyl in the phenolic acetates arises from Fermi resonance of a combination tone with the acetate carbonyl fundamental.

In phenyl acetate, the situation is complicated by the presence of three bands in the carbonyl region (Figure 1e), the relative intensities of which are dependent on solvent. We assume that these three bands arise from the mutual interaction of two combination tones with the carbonyl fundamental. Calculation of the unperturbed frequencies for a Fermi triad is considerably more involved than for the Fermi diad considered above and we accordingly report only the observed values.

The integrated intensity of the anthraquinone carbonyl band in the anthraquinone acetates studied appears to be independent of substitution, whilst the intensity of the acetate carbonyl is simply additive and may be used to determine the number of acetate groups on an anthraquinone nucleus. In this respect, it should be noted that the ratio of the acetate carbonyl intensity to the anthraquinone carbonyl intensity (0·813) is even more useful and allows the determination of the degree of acetylation of an anthraquinone in mixtures with other materials.

In some of the solutions of the anthraquinone acetates studied, the anthraquinone carbonyl band was unsymmetrical and suggested the presence of a medium-strong component on the low-frequency side of the band separated by ~4 cm.$^{-1}$ from the main component (Table). This is to be expected of those molecules not possessing a centre of symmetry.

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[7] H. W. Thompson and P. Torkington, *J.*, 1945, 640.

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