22. *Infrared Spectra of Aryl Carboxylic Acids and Their Esters.*

By C. J. W. Brooks, G. Eglinton, and J. F. Morman.

Regularities in carbonyl stretching frequencies for the series Ar·COX [X = Me, OH (dimer), H, OEt, OMe, and OH (monomer)] are briefly discussed. Data (ν, $\Delta\nu_{\frac{1}{2}}{}^{a}$, and ε_a) are presented for the carbonyl and hydroxyl stretching vibrations of 21 monosubstituted methyl benzoates and 23 monosubstituted benzoic acids in dilute solution (carbon tetrachloride). The frequency data for *meta*- and *para*-substituted derivatives correlate well with the relative acidity values reported by Davis and Hetzer.[1]

Methyl *o*-halogeno- and *o*-methoxy-benzoates and the corresponding acids exhibit split carbonyl bands, ascribed to conformational isomerism rather than to Fermi resonance. Selected compounds have been studied in several solvents (n-hexane, carbon disulphide, chloroform, acetonitrile, and ether–carbon tetrachloride).

This paper reports part of a general attempt to relate spectroscopic data to molecular structures and conformations. It describes infrared spectroscopic studies of a series of monosubstituted benzoic acids and the corresponding methyl esters. Previous investigations include those of Flett,[2] Goulden,[3] O'Sullivan and Sadler,[4] and Thompson and his co-workers.[5,6] Peltier *et al.*[7] have recently reported frequency data for some of the compounds examined: the complex absorption now shown to be exhibited by certain *ortho*-substituted benzoates was not disclosed by their work or by that of Forbes, Knight, and Coffen.[8]

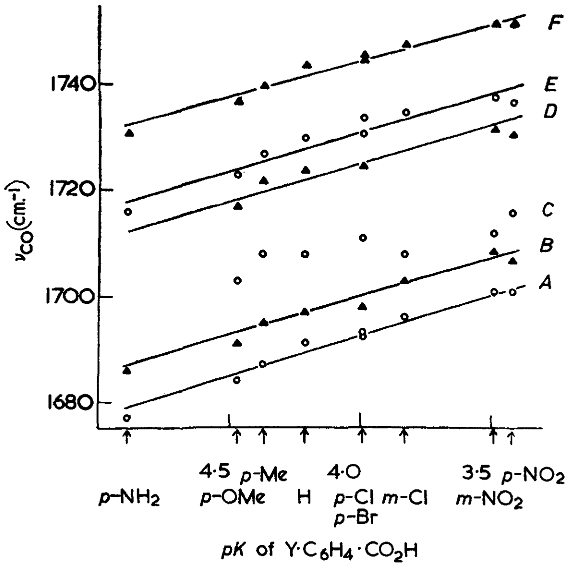

Fig. 1. *Carbonyl stretching frequencies* (CCl_4) *of* $Y{\cdot}C_6H_4{\cdot}COX$, *and* (*abscissa*) pK_a *of* $Y{\cdot}C_6H_4{\cdot}CO_2H$ (*ref.* 1). (*A*) *Aryl methyl ketones* (X = Me).[a, b] (*B*) *Aryl carboxylic acids* (X = OH: *dimers*).[b] (*C*) *Aryl aldehydes* (X = H).[b] (*D*) *Ethyl esters of aryl carboxylic acids* (X = OEt).[b] (*E*) *Methyl esters of aryl carboxylic acids* (X = OMe).[b] (*F*) *Aryl carboxylic acids* (X = OH: *monomers*).[b]

[a] Jones, Forbes, and Mueller, *Canad. J. Chem.*, 1957, **35**, 504. [b] Present work.

It is well known that carbonyl stretching vibrations can be treated as dependent

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[1] Davis and Hetzer, *J. Res. Nat. Bur. Stand.*, 1958, **60**, 569.

[2] Flett, *Trans. Faraday Soc.*, 1948, **44**, 767.

[3] Goulden, *Spectrochim. Acta*, 1954, **6**, 129.

[4] O'Sullivan and Sadler, *J.*, 1957, 2839.

[5] Thompson, Needham, and Jameson, *Spectrochim. Acta*, 1957, **9**, 208.

[6] Krueger and Thompson, *Proc. Roy. Soc.*, 1959, *A*, **250**, 22.

[7] Peltier, Pichevin, Dizabo, and Josien, *Compt. rend.*, 1959, **248**, 1148; Josien, Peltier, and Pichevin, *ibid.*, 1960, **250**, 1643.

[8] Forbes, Knight, and Coffen, *Canad. J. Chem.*, 1960, **38**, 728.

principally on the immediate environment of the group concerned.[9] From Fig. 1, in which correlations of the type due to Fuson, Josien, and Shelton,[10] Thompson *et al.*,[5] and Peltier *et al.*[7] are applied to our data, it is clear that the frequency separations (in carbon tetrachloride) between an aryl methyl ketone (Ar•COMe) and the corresponding compounds of the types $(Ar{\cdot}CO_2H)_2$, $Ar{\cdot}CO_2Et$, $Ar{\cdot}CO_2Me$, and $Ar{\cdot}CO_2H$ remain essentially constant at 7, 34, 39, and 52 cm.$^{-1}$, respectively, in the group of *meta-* and *para*-substituted derivatives considered. Systematic deviations from linearity, disclosed by the data now determined, are ascribed to factors (*e.g.*, the varying effects of solvation) tacitly assumed constant in plotting ν_{CO} (CCl_4) against p*K* (aqueous). The marked elevation of frequency in monomeric carboxylic acids as compared with the methyl ketones may be attributed to the strong electron-withdrawing power of the hydroxyl group.[11]

EXPERIMENTAL

Materials.—Most of the acids were obtained commercially. 6-Chlorosalicylic acid was kindly supplied by Dr. J. F. J. Dippy. *o*-Allyloxybenzoic acid, m. p. 58—59°, was prepared according to Nummy and Tarbell's directions [12] and *o*-hydroxymethylbenzoic acid, m. p. 131—133°, from phthalide. Methyl esters were prepared with diazomethane. All samples were carefully purified, finally by sublimation or short-path distillation at 0·1 mm. (with the exception of *o*-hydroxymethylbenzoic acid). M. p.s of solids agreed with recorded values,[13] except that of methyl *p*-chlorobenzoate (34—35°; lit.,[13] 44°). The purity of all liquid samples and of methyl *p*-chlorobenzoate was checked by gas–liquid chromatography using the Pye " Argon Chromatograph." Columns (46" × 1/5") were of Apiezon L (5%) on Celite 545 (120—150 mesh). Column temperature was 175°, flow rate 35 ml./min., and exit pressure 760 mm. Carbon tetrachloride, carbon disulphide, and n-hexane (all " AnalaR ") were used without purification. Chloroform (" AnalaR ") was freed from ethanol by two successive passages through blue silica gel immediately before use. The ether (sodium-dried)–carbon tetrachloride solutions were examined immediately after preparation. Acetonitrile was purified by successive prolonged treatments with potassium hydroxide, calcium chloride, and phosphorus pentoxide, followed by distillation.

Measurements.—Spectra were recorded linearly in cm.$^{-1}$ as percentage transmission with a Unicam S.P. 100 double-beam infrared spectrometer equipped with an S.P. 130 sodium chloride prism-grating double monochromator [1500 lines per inch (650—2000 cm.$^{-1}$) and 3000 lines per inch (2000—3656 cm.$^{-1}$)] operated under dry-air conditions. Below 650 cm.$^{-1}$ the instrument was operated as a potassium bromide prism monochromator. The cell-well temperature was 29° ± 3°. The wave-number scale was calibrated against methane, water vapour, carbon dioxide, and ammonia.[14] The calibration was checked before and after each uninterrupted group of measurements by using the water vapour bands at 3566 and 3586 cm.$^{-1}$ and a solution of acetone in carbon tetrachloride (band at 1719 cm.$^{-1}$). Measurements are believed accurate to ±1 cm.$^{-1}$. The linearity of the percentage transmission scale was checked by Shrewsbury's procedure,[15] and all intensity measurements were made on bands of at least 10% transmission. The theoretical spectral slit-width, computed from tables supplied by Messrs. Unicam Instruments Ltd., was approximately 4 cm.$^{-1}$ at 3500 cm.$^{-1}$, 4·5 cm.$^{-1}$ at 1650 cm.$^{-1}$, 5·2 cm.$^{-1}$ at 1750 cm.$^{-1}$, and 4 cm.$^{-1}$ at 650 cm.$^{-1}$. Carbonyl and hydroxyl bands were scanned at 18 cm.$^{-1}$ per min. for carbon tetrachloride, carbon disulphide, and chloroform solutions, and at 12 cm.$^{-1}$ per min. for ether–carbon tetrachloride, n-hexane, and acetonitrile solutions. The region 400—700 cm.$^{-1}$ was scanned at 27 cm.$^{-1}$ per min. The frequency values given are the mean of at least two determinations. Unless specified otherwise peaks are symmetrical: the apparent half-band widths ($\Delta\nu_{\frac{1}{2}}{}^{a}$) are quoted to the nearest integer. Intensities are given as apparent extinction coefficients ε_a (l. mole^{-1} cm.$^{-1}$) rounded to the nearest 5 units and measured from

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[9] Hartwell, Richards, and Thompson, *J.*, 1948, 1436; Bellamy, " The Infrared Spectra of Complex Molecules," Methuen & Co. Ltd., London, 2nd edn., 1958, Chapter 23.

[10] Fuson, Josien, and Shelton, *J. Amer. Chem. Soc.*, 1954, **76**, 2526.

[11] Taft, *J. Chem. Phys.*, 1957, **26**, 93.

[12] Nummy and Tarbell, *J. Amer. Chem. Soc.*, 1951, **73**, 1500.

[13] Heilbron and Bunbury, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, revised edition, 1953.

[14] Downie, Magoon, Purcell, and Crawford, *J. Opt. Soc. Amer.*, 1953, **43**, 941.

[15] Shrewsbury, " Unicam Spectrovision," 1958, No. 6, 1.

a solvent–solvent base-line superimposed on the record of the absorption of the solution (determined with solvent in the reference beam). Full spectra (3650—400 cm.$^{-1}$) of certain substituted methyl benzoates will appear in the D.M.S. Index (Butterworths) as spectral cards numbers 6227 onwards.

RESULTS AND DISCUSSION

Methyl Esters.—The results (CCl_4) are collected in Table 1. Single bands have been reported for *ortho*-substituted methyl [7] and ethyl [6] benzoates. With improved resolution it is now found that, while methyl *o*-methyl-, *o*-nitro-, and *o*-acetoxy-benzoate exhibit single sharp peaks, methyl *o*-halogeno-, *o*-methoxy-, and *o*-allyloxy-benzoates present two carbonyl bands separated to various degrees. This is not due to intermolecular effects, since dilution studies have shown that the relative intensities of the bands are independent of concentration. The band splitting observed in carbon tetrachloride solutions is more clearly defined in hexane (Fig. 2 and Table 2).

Of the two explanations which merit consideration for these effects, *viz.*, conformational equilibria or Fermi resonance, we favour the former in view of the evidence adduced below (see p. 114). We accordingly assign the band near 1730 cm.$^{-1}$ in the *o*-halogenobenzoates to conformation (Ia; X = Hal), and that near 1740 cm.$^{-1}$ to (Ib; X = Hal). (The ester group is depicted in the normally preferred conformation.[16]) Coplanarity of the substituents and the nucleus is not implied in these representations, the precise definition of which must await further evidence (*e.g.*, dipole-moment data). The higher-frequency band is associated with the alignment of carbonyl and C–halogen dipoles by analogy with α-halogeno-carbonyl compounds (*e.g.*, ketones,[17] aldehydes,[18] and esters [17,19,20]). The changes in the relative intensity of the two bands through the series *o*-F to *o*-I are most

TABLE 1. *Methyl esters of monosubstituted benzoic acids (in* CCl_4*)*.[b]

	m- and *p*-Substituents					*o*-Substituents			
No.		ν_{CO}	$\Delta\nu_{\frac{1}{2}}^{a}$	ε_a	No.		ν_{CO}	$\Delta\nu_{\frac{1}{2}}^{a}$	ε_a
1	*m*-NMe_2	1727	15	680	13	*o*-OMe	(1745sh) †	*	*
							1736	*	430
							1718	(25)	265
2	*m*-OMe	1728	15	660					
3	None	1730	11	900	14	*o*-Allyloxy	(1748sh) †	*	*
							1737	*	450
							1718	(23)	260
4	*m*-F	1733	11	795	15	*o*-Me	1728	13	710
5	*m*-Cl	1735	11	915	16	*o*-F	1741	(12)	315
							1726	14	510
6	*m*-Br	1734	11	850					
7	*m*-NO_2	1738	10	890	17	*o*-Cl	1744	13	410
							1727	(22)	240 †
8	*p*-OMe	1723	16	725	18	*o*-Br	1744	12	465
							1727sh	*	(195) †
9	*p*-F	1732 ‡	11	775					
10	*p*-Cl	1731	11	920	19	*o*-I	1740	12	550
							(1727sh)	*	(160) †
11	*p*-Br	1734 ‡	12	820	20	*o*-NO_2	1747	14	710
12	*p*-NO_2	1737	12	750	21	*o*-OAc [c]	1733	12	865

Compounds Nos. 4, 5, 9, and 10 showed $\nu_{max.}$ in CS_2 1—2 cm.$^{-1}$ lower than the values for CCl_4 solutions, with $\Delta\nu_{\frac{1}{2}}^{a}$ 9 ± 1 cm.$^{-1}$. Values in parentheses are approximate. sh = shoulder.

* Not measured. † Estimated by band reflection. ‡ Unsymmetrical band.

[b] Measured as approximately 0·0015M-solutions in 5 mm. cells. [c] Acetate-carbonyl absorption at 1775 cm.$^{-1}$ ($\Delta\nu_{\frac{1}{2}}^{a}$, 16; ε_a, 530).

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[16] Mizushima, " Structure of Molecules and Internal Rotation," Academic Press Inc., New York, 1954, pp. 88, 89.

[17] Bellamy and Williams, *J.*, 1957, 4294.

[18] Bellamy and Williams, *J.*, 1958, 3465.

[19] Josien and Calas, *Compt. rend.*, 1955, **240**, 1641; Josien and Castinel, *Bull. Soc. chim. France*, 1958, 801.

[20] Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 3513.

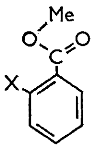
TABLE 2. *Methyl benzoate, methyl* o-*methoxybenzoate, and methyl* o-*halogenobenzoates in various solvents.*

Solvent	No.	Subst.	Absorption bands in carbonyl region					
			ν_{CO}	$\Delta\nu_{\frac{1}{2}}$[a]	ε_a	ν_{CO}	$\Delta\nu_{\frac{1}{2}}$[a]	ε_a
n-Hexane [b]	3	None	—	—	—	1735	9	1035
	13	*o*-OMe	1745	14	395	1723	16	305
	16	*o*-F	1749	9	260	1731	9	425
	17	*o*-Cl	1750	8	465	1733	14	285
	18	*o*-Br	1750	8	550	1735	18	240 †
	19	*o*-I	1746	8	630	1736sh	*	(200) †
Acetonitrile [c]	3	None	—	—	—	1724	11	790
	13	*o*-OMe	1731	16	505	(1709sh)	*	(105) †
	16	*o*-F	1733	12	520	1723	13	425 †
	17	*o*-Cl	1736	18	480	(1724sh)	*	(120) †
	18	*o*-Br	1737	(16)	535	(1729) §	*	(135) †
	19	*o*-I	1733	(15)	540	(1725) §	*	(85) †
Carbon disulphide [d]	3	None	—	—	—	1728	8	*
	13	*o*-OMe	1735	(15)	*	1713	24 †	*
	16	*o*-F	1739	(11)	*	1724	12	*
	17	*o*-Cl	1743	(13)	*	1726	(16)	*
	18	*o*-Br	1741	11 †	*	(1725) §	*	*
	19	*o*-I	1738	9 †	*	(1725) §	*	*

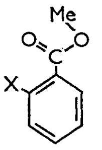
— No band present. § Concealed band. For other symbols see Table 1.
[b] *Ca.* 0·0076M-, [c] *ca.* 0·019M-, [d] *ca.* 0·015M-solutions; all in 0·5 mm. cells.

simply rationalised (the intensities being taken as approximately indicative of concentrations) in terms of the size of the halogen atom, the small fluorine atom permitting a preponderance of (I*a*; X = F) in the equilibrium mixture. For methyl *o*-methoxybenzoate in hexane the bands at 1723 and 1745 cm.$^{-1}$ are ascribed to conformations (Ia and Ib; X = OMe) respectively by analogy with the *o*-halogeno-esters and with the assignments made by T. L. Brown [20] for ethyl ethoxyacetate.

Additional support for the conformational assignments made for the *o*-halogeno- and *o*-methoxy-benzoates was derived from measurements in acetonitrile (Table 2 and Fig. 2). The carbonyl frequencies are generally about 6 cm.$^{-1}$ lower than in carbon tetrachloride. In each example, the intensity of the higher-frequency band is relatively higher in acetonitrile (and the lower-frequency band becomes less and less distinct in the series *o*-F, *o*-Cl, *o*-Br, and *o*-I; Fig. 2). Bellamy and Williams [17] observed a similar effect in α-chloroketones, and pointed out that intensification of the higher-frequency band in the more polar solvent supported its assignment to the more polar conformation. Brown [20] has reported similar results for ethyl chloro- and dichloro-acetate in chloroform and acetonitrile as compared with carbon tetrachloride.



(Ia)



(Ib)

Methyl *o*-nitrobenzoate shows only a single (slightly unsymmetrical) band in the carbonyl region. Possibly in this ester the methoxycarbonyl group is so displaced by the preferential coplanarity of the nitro-group that there is essentially only one conformation. Single bands are exhibited by methyl *o*-toluate and *o*-acetoxybenzoate. Evidently these weakly polar substituents do not induce markedly different ν_{CO} values in the two possible conformations (cf. ref. 21). Two disubstituted esters have been briefly examined. Methyl 2,6-dimethoxybenzoate shows a single carbonyl band in n-hexane (1750 cm.$^{-1}$; $\Delta\nu_{\frac{1}{2}}$[a]

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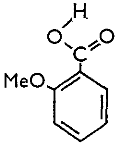
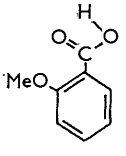
[21] Jones, Forbes, and Mueller, *Canad. J. Chem.*, 1957, **35**, 504; Jones, *Proc. Roy. Soc. Canada*, 1958, **52**, Ser. III, Sect. III, 9.

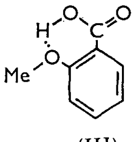
8 cm.$^{-1}$) and in carbon tetrachloride (1723 cm.$^{-1}$; $\Delta\nu_{\frac{1}{2}}{}^{a}$ 17 cm.$^{-1}$; ε_a 745). The remarkable solvent effects on the frequency and half-band width are presumably associated with the steric strain in this ester. Methyl 2,3-dimethoxybenzoate shows the expected split carbonyl band in n-hexane (1743 cm.$^{-1}$, $\Delta\nu_{\frac{1}{2}}{}^{a}$ ~11 cm.$^{-1}$, ε_a 440; 1729 cm.$^{-1}$, ε_a ~175) and, less clearly resolved, in carbon tetrachloride (1736 cm.$^{-1}$, $\Delta\nu_{\frac{1}{2}}{}^{a}$ ~18 cm.$^{-1}$, ε_a ~435; ~1721 cm.$^{-1}$, ε_a ~130) and in acetonitrile (1730 cm.$^{-1}$, $\Delta\nu_{\frac{1}{2}}{}^{a}$ ~16, ε_a 495; 1719 cm.$^{-1}$, ε_a ~95).

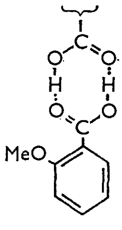
With regard to the intensities of carbonyl bands in substituted methyl benzoates, the apparent half-band widths and extinction coefficients (Tables 1 and 2) show no striking variations. Integrated intensity values (A) computed by Ramsay's method[22] ranged from 2·9 × 10^{4} (No. 9) to 4·1 × 10^{4} l. mole^{-1} cm.$^{-2}$ (No. 8). The values are based on single determinations and show no regularity. Thompson *et al.*[5] have demonstrated a linear relation between log A (by area integration) and σ for a group of six *meta*- and *para*-substituted ethyl benzoates. That the *ortho*-substituted esters did not conform[6] is not surprising in view of the complex absorption now disclosed.

Substituted Benzoic Acids.—Data for *meta*- and *para*-substituted acids (Table 3) indicate that the monomer carbonyl band ranges from 1737 to 1752 cm.$^{-1}$ and the dimer band from 1691 to 1709 cm.$^{-1}$. In the hydroxyl region the monomer band position is dependent on the substituent (and can be related[3] to the pK of the acid—see also below), while the dimer band is remarkably constant in appearance throughout the series examined. Data for nine *ortho*-substituted acids are tabulated. Of these, *o*-toluic, *o*-nitrobenzoic, and *o*-acetoxybenzoic acid exhibit single monomer carbonyl bands. In *o*-methoxybenzoic acid [the conformation of CO_2H is written as in (II) following Mizushima;[16] Davies[23] has depicted a hydrogen bond between the carbonyl and hydroxyl groups] the occurrence of the three species (II) [the two possible forms (IIa) and (IIb)[24] being treated as one], (III), and (IV) was demonstrated spectroscopically by Fox and Martin,[25] who showed that the hydroxyl stretching frequencies due to forms (II), (III), and (IV) in carbon tetrachloride solution were 3530, 3362, and *ca.* 2950 cm.$^{-1}$, respectively. We assign the carbonyl absorption as follows: the predominant form (III), 1751 cm.$^{-1}$; (IV) (three possible conformations), approx. 1703 cm.$^{-1}$. The shoulder observed near 1760 cm.$^{-1}$ may be tentatively ascribed to the small amount of form (II). It seems probable that the principal conformation of the dimer is (IV), as discussed further below.


(IIa)


(IIb)


(III)


(IV)

The series of *o*-halogeno-acids presents interesting features. The monomeric carbonyl bands parallel those of the methyl esters in showing two peaks. One is at a slightly lower frequency than that found for benzoic acid, the other is substantially higher. The separation of about 17 cm.$^{-1}$ between the peaks remains essentially constant throughout the series, but the relative intensities (ε_a) change progressively from *o*-F ($\varepsilon_{1755}/\varepsilon_{1739}$ = 0·70) to *o*-I ($\varepsilon_{1753}/\varepsilon_{1736} \approx$ 3·3), as indicated in Fig. 2. The attribution of both peaks to monomeric forms was confirmed in every case by dilution studies. In the hydroxyl absorption region the spectra of the *o*-halogeno-acids are almost indistinguishable from those of the *meta*- and *para*-isomers, except in the exact position of the monomer band near 3530 cm.$^{-1}$.

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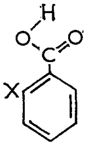
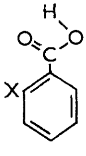
[22] Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.
[23] Davies, in "Hydrogen Bonding," Pergamon Press, London, 1959, p. 393.
[24] Davies and Griffiths, *J.*, 1955, 132.
[25] Fox and Martin, *Nature*, 1939, **143**, 199.

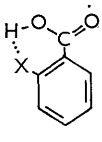
The observed absorption bands near 1738 and 1755 cm.$^{-1}$ are consequently attributed to the conformational isomers (Va; X = Hal) and (Vb; X = Hal) and the absorption near 1700 cm.$^{-1}$ to the three possible dimeric forms derived therefrom. We believe that the dimers exist principally in the conformation (VI; X = Hal) since (i) the frequency



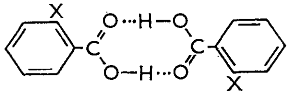
(Va)
(lower-frequency band)



(Vb)
(higher-frequency band)



(Vc)



(VI)

separations between the carbonyl bands attributed to (Vb) and the corresponding dimer bands have values close to those (~45 cm.$^{-1}$) found for all the other substituted benzoic acids examined; (ii) in the crystalline state, *o*-chlorobenzoic and *o*-bromobenzoic acid exist as depicted in (VI), as demonstrated by *X*-ray crystallographic studies (personal communication from Dr. G. A. Sim and Mr. G. Ferguson, The Chemistry Department, Glasgow University). Solid state spectra of the acids were not informative.

Intramolecular hydrogen bonding (Vc; X = Hal) in *o*-halogenobenzoic acids has been frequently postulated (*e.g.*, refs. 1, 8, 26, but cf. 27). However, the single, closely similar monomer hydroxyl bands observed for the four *o*-halogeno-acids in carbon tetrachloride or chloroform solutions are incompatible with this proposal. [In the *o*-halogenophenols (hydrogen bond in 5-membered ring) ν_{OH} ranges[28] from 3584 (*o*-F) to 3500 (*o*-I) cm.$^{-1}$.] Possibly hydrogen bonding is inhibited in the *o*-halogeno-acids by steric displacement of the carboxyl group due to repulsion between the halogen and hydroxylic oxygen atoms. In support of this we note that in 6-chlorosalicylic acid, in which proximity and coplanarity of the halogen and hydroxylic oxygen atoms are both enforced by the chelation of the remaining groups, two bands, at 3508 cm.$^{-1}$ (free) and 3430 cm.$^{-1}$ (bonded), are observed.

Absorption data for solutions of *o*-methoxybenzoic acid and of the *o*-halogenobenzoic acids in chloroform and in mixtures of ether and carbon tetrachloride are recorded in Tables 4 and 5. The splitting of the monomer carbonyl absorption is not obvious in chloroform (*e.g.*, Fig. 3), an effect partly attributable to the usual band-broadening induced by this solvent. The molecular species involved are doubtless solvated monomers, since the frequencies are markedly displaced (—7 to —17 cm.$^{-1}$) from those observed in carbon tetrachloride, whereas the dimer absorption frequencies are almost unaltered. The monomer frequency shifts (ν_{CO} in CCl_4 minus ν_{CO} in $CHCl_3$) are of the same order as those we have observed for substituted methyl benzoates (*p*-NO_2, —11; *p*-Cl, —9; unsubstituted, —10; *m*-NMe_2, —10 cm.$^{-1}$: the effect of the substituents on the polarity of the carbonyl linkage is not evident). We regard the similarity of the dimer frequencies in chloroform and carbon tetrachloride as due to the virtual elimination of the basicity of the carbonyl group consequent upon dimer formation (cf. refs. 29, 30). Cole and Michell[31] have proposed an explanation based on steric shielding. The single frequencies recorded by O'Sullivan and Sadler[4] for these acids in chloroform appear to correspond approximately to our dimer frequencies.

The results for ether–carbon tetrachloride solutions (*e.g.*, Fig. 3) parallel those for

[26] Kilpatrick and Mears, *J. Amer. Chem. Soc.*, 1940, **62**, 3051; Ito, Tsukioka, and Imanishi, *ibid.*, 1960, **82**, 1559.

[27] McDaniel and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 3756.

[28] Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 3598.

[29] Cannon, *Mikrochim. Acta*, 1955, 555.

[30] Bellamy and Williams, *Proc. Roy. Soc.*, 1960, *A*, **255**, 22.

[31] Cole and Michell, *J.*, 1959, 2005.

carbon tetrachloride in respect of (i) the splitting of the monomer absorption bands [ether-bonded monomer ($Ar{\cdot}CO_2H \cdots OEt_2$) in this case], (ii) the frequency separation of about 16 cm.$^{-1}$ between the bands, and (iii) the change in relative intensities through the sequence *o*-F, *o*-Cl and *o*-Br. The frequency shifts (about 18 cm.$^{-1}$) parallel those observed for dioxan [32] as compared with carbon tetrachloride.[2] In both cases the effect is due to the mitigation of the electron-withdrawing character of the carboxylic OH group by hydrogen-bonding to the ether oxygen atom: the frequencies of carbonyl groups *per se* are only slightly affected by ether as compared with carbon tetrachloride [*e.g.*, acetophenone, 1694 (ether) and 1692 (carbon tetrachloride) cm.$^{-1}$].[30] Cole and Michell [31] have reported for benzoic acid, in dioxan, carbonyl bands at 1723 and 1636 cm.$^{-1}$, which they ascribe respectively to monomer and to a hydrogen-bonded benzoic acid–dioxan complex. We observe no carbonyl band near 1636 cm.$^{-1}$ for benzoic acid in ether–carbon tetrachloride: the absorption reported is probably a result of loss of spectrometer energy by solvent absorption. We assign the band at 1723 cm.$^{-1}$ to the dioxan-bonded monomeric acid. In Table 5 data are recorded for the carbonyl absorption of *o*-methoxybenzoic acid in ether–carbon tetrachloride. With increasing concentrations of ether the intensity of the band

TABLE 3. *Monosubstituted benzoic acids* (*in* CCl_4).[b]

No.	Subst.	Monomer			Dimer			Monomer[c, d]	
		ν_{CO}	$\Delta\nu_{\frac{1}{2}}^{a}$	ε_a	ν_{CO}	$\Delta\nu_{\frac{1}{2}}^{a}$	ε_a	ν_{OH}	$\Delta\nu_{\frac{1}{2}}^{a}$
22	*m*-NMe_2	1740	14	245	1693	15	660	3541	29
23	*m*-OMe	1741	13	215	1698	17	640	3539	30
24	*m*-Me	1742	13	260	1698	14	805	3540	27
25	None	1744	13	270	1697 ‡	16	750	3540	27
26	*m*-F	1748	11	270	1703	13	685	3536	30
27	*m*-Cl	1748	12	285	1703	16	700	3535	30
28	*m*-Br	1748	12	275	1702	14	685	3535	31
29	*m*-NO_2	1752	10	305	1709	18	575	3530	35
30	*p*-OMe	1737	13	*	1691	12	*	3542	25
31	*p*-Me	1740	12	265	1697 ‡	12	995	3541	26
32	*p*-F	1745	13	255	1699	12	880	3538	30
33	*p*-Cl	1745	11	*	1698 ‡	10	*	3536	32
34	*p*-Br	1746	13	*	1698	16	*	3536	32
35	*p*-NO_2	1752	13	*	1707	15	*	3529	*
36	*o*-OMe	(1760sh)	*	*	1702 ¶	*	*	3530	40
		1751	14	670				3365	80
37	*o*-Allyloxy	1751	15	880	1703	*	*	3529	38
								3354	90
38	*o*-Me	1742 ‡	16	250	1696 ‡	18	590	3538	30
39	*o*-F	1755	12	155	1707	23	535	3529	32
		1739	*	220	(1700sh)	*	*		
40	*o*-Cl	1756	12	200	1706	25	440	3527	38
		1738	*	(105) †					
41	*o*-Br	1757	12	200	1711 ‡	26	420	3528	38
		1738	*	(95) †					
42	*o*-I	1753	12	230	1708 ‡	22	465	3530	38
		(1736sh)	*	(90) †					
43	*o*-NO_2	1760	16	*	1715	19	*	3520	35
44	*o*-OAc [e]	1747 ‡	14	395	1702	18	545	3532	35

¶ Very weak band: $\nu_{max.}$ confirmed by measurement at higher concentration. For other symbols see Table 1.

[b] Measured as 0·00150 ± 0·00002M-solutions [except for Nos. 36 (0·0018M) and 30, 33, 34, 35, and 43 (saturated solutions)] in 5 mm. cells (ν_{CO}) or 20 mm. cells (ν_{OH}). [c] In the region 3650—2500 cm.$^{-1}$ the following additional assignments were made: No. 22, 2807 cm.$^{-1}$ (ν_{CH},NMe);[f] Nos. 23 and 30, 2835 and 2841 cm.$^{-1}$ respectively (ν_{CH},OMe).[g] No. 36 showed no sharply defined peak attributable to the latter vibration. Nos. 36 and 37 showed a weak band near 3475 cm.$^{-1}$ presumed to be the first overtone of the intense carbonyl band at 1751 cm.$^{-1}$. [d] ε_a for ν_{OH} was virtually constant at about 50 cm.$^{-1}$, except for Nos. 36 and 37 for which ε_a values were: No. 36, 15 and 100 cm.$^{-1}$; No. 37, 10 and 105 cm.$^{-1}$. [e] Acetate carbonyl at 1776 cm.$^{-1}$ ($\Delta\nu_{\frac{1}{2}}^{a}$ 15, ε_a 505). [f] Hill and Meakins, *J.*, 1958, 760. [g] Henbest, Meakins, Nicholls, and Wagland, *J.*, 1957, 1462.

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[32] Flett, *J.*, 1951, 962.

FIG. 2. *Carbonyl absorptions of benzoic acid, methyl benzoate and* o-*substituted derivatives in various solvents.* (A) CCl_4; (B) $CHCl_3$; (C) *n-hexane*; (D) MeCN. *The relevant concentrations and path lengths are as given in Tables* 1, 2, *and* 3 *except for B* (0·0015M-*solution in* 5 *mm. cells*).

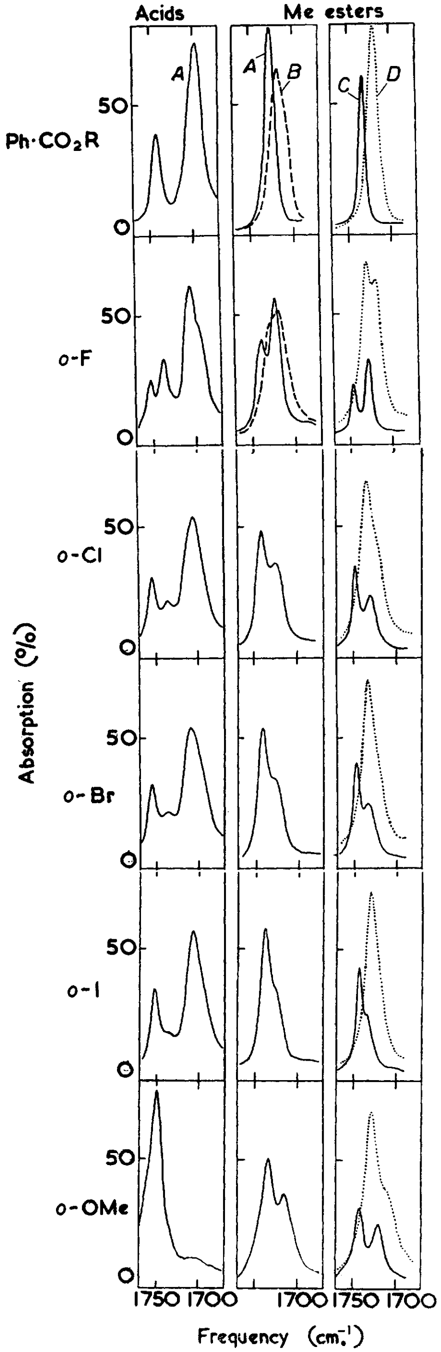


FIG. 3. *Carbonyl absorption of* o-*fluorobenzoic acid in* (*A*) CCl_4, (*B*) 8% (v/v) *ether*–CCl_4, *and* (*C*) $CHCl_3$. *Solutions are* 0·0015M *in* 5 *mm. cells.*

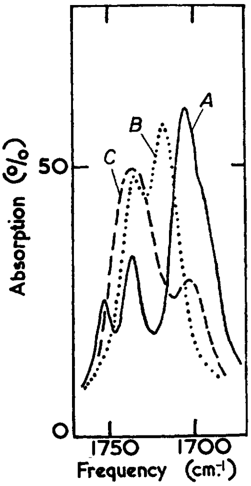
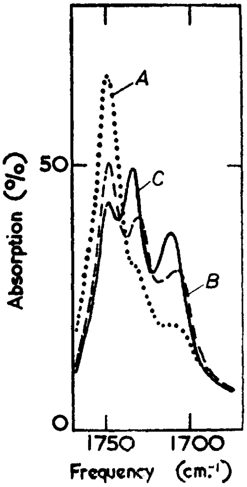


FIG. 4. *Carbonyl absorption of* o-*methoxybenzoic acid in ether*–CCl_4 *mixtures.* (*A*) 0·0015M *in* 4% (v/v) Et_2O–CCl_4: 5 *mm. cells.* (*B*) 0·015M *in* 20% (v/v): 0·5 *mm.* (*C*) 0·015M *in* 100% Et_2O: 0·5 *mm.*



associated with the intramolecularly bonded conformation (III) is markedly reduced, finally to less than half the value in carbon tetrachloride. Fig. 4 illustrates the latter trend and also shows the emergence of two new carbonyl bands (at approximately 1715 and 1735 cm.$^{-1}$). These are attributed to the ether-bonded forms corresponding to the two conformations (IIa) and (IIb). The possibility that the band near 1715 cm.$^{-1}$ is due to a dimeric form is rejected since it increases in intensity with increasing ether concentration.

At approximately equimolar concentrations the ratio of monomer to dimer increases through the sequence of solvents, n-hexane, carbon tetrachloride, carbon disulphide, chloroform, and acetonitrile. Even at high concentrations (~1M, 0·05 mm.) in acetonitrile, benzoic acid shows negligible dimer absorption. *o*-Fluorobenzoic acid gives two monomer carbonyl bands in n-hexane and in acetonitrile: in the latter solvent they are of equal intensity. The carbonyl absorption of *o*-methoxybenzoic acid is relatively unaffected by the solvent: this is explicable in terms of the stability of form (III). Typical data (wave-numbers in cm.$^{-1}$) are assembled below.

TABLE 4. *Benzoic acid and* o-*substituted benzoic acids.*[b]

		Chloroform							Ether–CCl$_4$ (20 : 80 v/v)		
		Monomer			Dimer			Monomer	Bonded monomer		
No.	Subst.	ν_{CO}	$\Delta\nu_{\frac{1}{2}}{}^a$	ε_a	ν_{CO}	$\Delta\nu_{\frac{1}{2}}{}^a$	ε_a	ν_{OH}	ν_{CO}	$\Delta\nu_{\frac{1}{2}}{}^a$	ε_a
25	None	1734	25	360	1697	20	235	3524	1726	15	720
39	*o*-F	1738	34	375	1706	(25)	(195)	3514	1737	17	355
									1721	17	485
40	*o*-Cl	1744 ‡	30	380	1706	(28)	(170)	3512	1738	14	465
									1720	*	(190) †
41	*o*-Br	1743	25	395	1706	(24)	(160)	3512	1737	13	450
									(1722sh)	*	(150) †
42	*o*-I	1746 ‡	30	355	1709	(38)	(155)	3509	*	*	*
45	*o*-CH_2OH	1721	*	*	1687	*	*	3515	*	*	*

For symbols see Table 1. [b] Measured as 0·0015M-solutions in 5 mm. cells ($CHCl_3$), except No. 45 (saturated solution), and in 2 mm. cells (ether–CCl_4).

TABLE 5. *Carbonyl bands of monomeric forms of* o-*methoxybenzoic acid in ether–carbon tetrachloride.*

			Monomer (III)		Ether-bonded monomer			
					(IIb)?		(IIa)?	
Molarity	Cell path (mm.)	Ether (% v/v)	ν_{CO}	ε_a	ν_{CO}	ε_a	ν_{CO}	ε_a
0·0018	5·0	0	1751	670	—	—	—	—
0·0015	5·0	4	1752	630	(1735sh)	*	(1710)	*
0·015	0·5	20	1751	405	1734	(265)	1712	(205)
0·015	0·5	50	1751	(325)	1735	(345)	1714	(240)
0·015	0·5	100	1752	(315)	1738	(385)	1715	(260)

For symbols see Table 1.

	Solvent				Solvent		
Sub-stituent	n-Hexane		Acetonitrile	Sub-stituent	n-Hexane		Acetonitrile
	$\nu_{CO(monomer)}$	$\nu_{CO(dimer)}$	$\nu_{CO(monomer)}{}^a$		$\nu_{CO(monomer)}$	$\nu_{CO(dimer)}$	$\nu_{CO(monomer)}{}^a$
None ...	1750	1703	1727	*o*-I	*	*	1736
o-F	1762	1710	1738	*o*-OMe ...	1759	(1707)	1739
	1746	(1698sh)	1726		(1763sh)		

[a] Half-band widths ($\Delta\nu_{\frac{1}{2}}{}^a$) 20 ± 2 cm.$^{-1}$. Values in parentheses are approximate.
* Not measured. sh = shoulder.

Evidence relating to Conformational Assignments.—In recent papers [33,34] R. N. Jones and his colleagues have pointed out that solvent- and temperature-dependent modifications

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[33] Angell, Krueger, Lauzon, Leitch, Noack, Smith, and Jones, *Spectrochim. Acta*, 1959, 926.
[34] Jones, Angell, Ito, and Smith, *Canad. J. Chem.*, 1959, **37**, 2007.

of carbonyl frequencies, though often attributed to conformational equilibria, can be produced by Fermi resonance and other vibrational interactions. The principal evidence in support of our conformational interpretations is as follows:

(*a*) The retention of regular absorption patterns (Figs. 2 and 3 and Tables 2, 3, and 4) by the methyl *o*-halogenobenzoates in n-hexane and carbon tetrachloride, and by the corresponding carboxylic acid monomers in carbon tetrachloride and ether–carbon tetrachloride, seem unlikely to result from Fermi resonance.

TABLE 6. *Frequency shifts* ($\Delta\nu = \nu_{\text{hexane}} - \nu_{\text{solvent}}$) *and approximate relative intensities of " split " carbonyl bands* [a] *in various solvents.*

	n-Hexane [d]		CCl_4 [e]		CS_2 [e]		MeCN [d]	
	ν	$\varepsilon_1/\varepsilon_2$	$\Delta\nu$	$\varepsilon_1/\varepsilon_2$	$\Delta\nu$	$\varepsilon_1/\varepsilon_2$	$\Delta\nu$	$\varepsilon_1/\varepsilon_2$
Methyl benzoate	1735	—	5	—	7	—	11	—
Methyl *o*-fluorobenzoate	1749	0·61	8	0·62	10	0·72	16	1·22
	1731		5		7		8	
Methyl *o*-chlorobenzoate	1750	1·64	6	1·70	7	1·70	14	4·0
	1733		6		7		9	
Methyl *o*-methoxybenzoate ...	1745	1·3	9	1·62	10	1·70	14	4·8
	1723		5		8		14	
Benzoic acid [b]	1750	—	6	—	9	—	23	—
o-Fluorobenzoic acid [b]	1762	0·71	6	0·70	9	0·73	24	1·0
	1746		5		8		20	
Coumarin	1759	3·2	4	0·84	6	0·75	4	0·26
	1746		3		5		11	
Cyclopentanone	1755	(15)	5	(7)	7	(7)	10	1
	1724 †		−3 †		−2 †		−11	
Cyclohexanone [c]	1724	—	5	—	7	—	15	—

[a] In the $\Delta\nu$ columns the upper figures refer to the higher-frequency bands ν_1. [b] Monomer bands. In 20% v/v ether–CCl_4 benzoic acid has $\Delta\nu = 24$ cm.$^{-1}$; *o*-fluorobenzoic acid has $\Delta\nu_1 = 25$, $\Delta\nu_2 = 25$ cm.$^{-1}$, and $\varepsilon_1/\varepsilon_2 = 0{\cdot}73$. The dimer carbonyl causes some interference in the hexane, CCl_4, and CS_2 solutions. [c] Data from ref. 33; $\Delta\nu$ values refer to $\nu_{\text{cyclohexane}}$. [d] 0·5 mm. cells. [e] 5 mm. cells.

(*b*) The regularly increasing preponderance of the higher frequency bands through the series of *ortho*-substituents H, F, Cl, Br, I parallels the trend already described in conformational terms for the *o*-halogenoacetophenones.[21] If Fermi resonance is invoked, *decreased* coupling would have to occur for a smaller frequency separation between the bands—the inverse of normal experience. Furthermore, there are no obvious frequencies (400 cm.$^{-1}$ upwards) which might be consistently employed to provide overtone or combination bands close to 1730 cm.$^{-1}$ in either the acids or their methyl esters.

(*c*) The solvent shifts (Table 6) of the split carbonyl bands in methyl *o*-fluoro-, *o*-chloro-, and *o*-methoxy-benzoates, and in *o*-fluorobenzoic acid, are not much different from the values observed for the unsubstituted compounds. On the other hand, in the examples (coumarin [34] and cyclopentanone [33,35]) ascribed to Fermi resonance, the solvent shifts are irregular, since neither of the observed fundamentals represents the simple carbonyl group frequency.[36] The ratio ($\varepsilon_1/\varepsilon_2$) of the intensities of the two bands (higher ν_1/lower ν_2) observed in Fermi resonance decreases markedly as the solvent polarity is increased. In the substituted benzoic acids and esters the reverse trend is clearly shown. Preliminary observations of the temperature dependence of the absorption of methyl *o*-fluorobenzoate in carbon tetrachloride indicate that, over the range 30—70°, the higher frequency band [attributed to (Vb; X = F)] becomes relatively more intense as the temperature rises: at 70° the ratio of intensities was 7% above that found at 30°, an effect consonant with our assignments. A study of deuterated compounds would be desirable.

(*d*) Where detectable conformational isomers are not expected, the carbonyl bands are

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[35] Allen, Ellington, and Meakins, *J.*, 1960, 1909.

[36] Brand and Speakman, " Molecular Structure," Edward Arnold, London, 1960, p. 154.

not split; *e.g.*, the *meta*- and *para*-substituted benzoic acids and esters and methyl 2,6-dimethoxybenzoate.

(*e*) Careful comparison of the spectra of the methyl *o*-halogenobenzoates as liquid films, and as solutions in carbon disulphide and acetonitrile, reveals that intensity changes parallel to those in the carbonyl region occur in at least two pairs of bands (near 1040 cm.$^{-1}$ and near 1260 cm.$^{-1}$) in the region 400—1600 cm.$^{-1}$. This behaviour is entirely consistent with the presence of two isomers. The *m*- and *p*-halogenobenzoates do not show these effects.

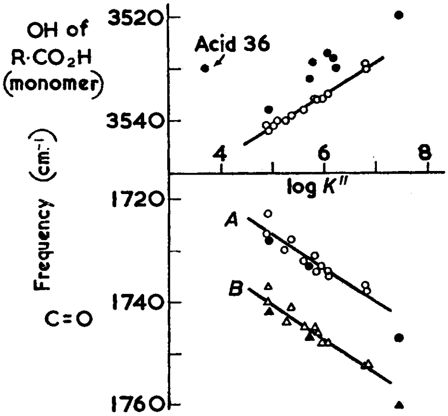

FIG 5. *Carbonyl and hydroxyl stretching frequencies* (CCl_4) *of aryl carboxylic acids and methyl esters, and* (*abscissa*) *log* K'' *for the neutralisation of the acids by diphenylguanidine in benzene* (*ref.* 1).

● ▲: ortho-*Substituted derivatives.*

A, R·CO_2Me; *B*, R·CO_2H (*monomer*).

Correlation of Frequencies with Acid Strengths.—Davis and Hetzer[1] have suggested that frequency data determined in relatively non-polar solvents might be better correlated with comparative acid strengths determined in similar solvents than with aqueous p*K*'s. A plot of this type is presented in Fig. 5. The monomer hydroxyl frequencies of the *meta*- and *para*-substituted acids are well accommodated, but the values for *ortho*-substituted acids are displaced, mostly to lower frequencies. We conclude that, although the use of non-aqueous acid strengths might appear desirable, yet it does not in this instance greatly improve the consistency already shown by the p*K* or σ values.

Plotting [2 log ε_a (monomer) — log ε_a (dimer)] against log *K''* affords evidence of a linear relation, in accordance with correlations previously suggested[37,1] between the equilibrium constants for dimer dissociation and for ionisation.

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[37] Allen and Caldin, *Quart. Rev.*, 1953, **7**, 255.