326. *Hydrogen Bonding in Pyrocatechol Monoesters and Related Compounds.*

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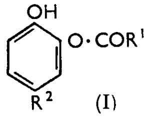
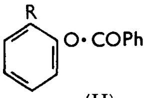
Infrared-spectroscopic examination of some pyrocatechol monoesters (I) and related compounds (III) has shown that they may exist as mixtures of conformers in carbon tetrachloride solution. These conformers involve various types of intramolecular hydrogen bond, including those requiring closure of 5-, 7-, and 9-membered rings. The effects of other solvents have been examined.

A reaction of value in determining the structure of the gallotannins is methanolysis [1,2] whereby *o*-hydroxy-depsides of the type (I) are split at the ester linkage by methanol at neutral pH. In this connexion we have studied the infrared spectra of compounds of this type and of related types (II and III) in several solvents, so as to determine the extent of interaction of the *o*-hydroxyl group with the ester linkage.



(I)



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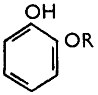

(III)

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[1] Armitage, Haslam, Haworth, Mills, Rogers, and Searle, *J.*, 1961, 1836.

[2] Armitage, Bayliss, Gramshaw, Haslam, Haworth, Jones, Rogers, and Searle, *J.*, 1961, 1842; Haslam, Haworth, and Keen, *J.*, 1962, 3814; Armitage, Haslam, Haworth, and Searle, *J.*, 1962, 3808.

EXPERIMENTAL

Materials.—The following *o*-hydroxyphenyl esters were prepared by published methods: 1-*O*-acetyl-[3] and 1-*O*-benzoyl-pyrocatechol[4] and methyl 3-*O*-benzoylprotocatechuate.[1] The remaining *ortho*-substituted phenylbenzoates were prepared by the Schotten–Baumann procedure from the phenols. 2-*o*-Hydroxyphenoxybenzophenone (V) and *o*-phenoxyphenol were kindly supplied by Dr. J. D. Loudon.[5] o-α-*Phenylbenzyloxyphenol*, b. p. 164—166°/1 mm., n_D^{21} 1·6116, (Found: C, 82·5; H, 6·3. $C_{19}H_{16}O_2$ requires C, 82·5; H, 5·9%), was obtained by hydrogenation of 2-*o*-hydroxyphenoxybenzophenone in ethanol over 10% palladised charcoal. The remaining compounds were of commercial origin. The compounds were purified by distillation or crystallisation, dried, and checked by thin-layer or gas–liquid chromatography before use. " AnalaR " carbon tetrachloride and spectroscopic-grade n-hexane were used without purification. " AnalaR " chloroform was dried several times by passage through a column of blue silica gel immediately before use. Acetonitrile was purified by prolonged treatment 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 spectrophotometer equipped with an S.P. 130 sodium chloride prism-grating double monochromator [3000 lines per inch (2000—3656 cm.$^{-1}$) and 1500 lines per inch (650—2000 cm.$^{-1}$)] operated under a vacuum. The calibration was checked against the spectrum of water vapour after each group of measurements. The hydroxyl and carbonyl absorptions were scanned at 4·6 and 8·0 cm.$^{-1}$ per min., respectively. Frequency measurements for the " free " and the intrabonded hydroxyl and carbonyl bands are believed to be accurate to ± 1 cm.$^{-1}$. The linearity of the percentage transmission scale was checked by Shrewsbury's procedure,[6] and intensities were measured on bands of not less than 10% transmission. The theoretical spectral slit-width, computed from tables supplied by Unicam Instruments Ltd., was ~5·5 cm.$^{-1}$ at 3600 cm.$^{-1}$, 4·5 cm.$^{-1}$ at 3350 cm.$^{-1}$, and 3·4 cm.$^{-1}$ at 1700 cm.$^{-1}$. Unless specified otherwise, peaks were symmetrical; the apparent half-band widths, $\Delta\nu_{\frac{1}{2}}^{a}$, are quoted to the nearest integer; where necessary they were determined by reflection of the undisturbed wings of the unsymmetrical bands. Intensities are given as apparent extinction coefficients, ε^{a}, (l. mole^{-1} cm.$^{-1}$) rounded to the nearest 5 units and measured from a solvent–solvent base-line superimposed on the record of the spectrum of the solution (determined with solvent in the reference beam).

RESULTS AND DISCUSSION

The effect of *ortho*-substitution in phenyl benzoate by groups other than hydroxyl was first examined (type II; Table 1) and, in general, a small increase in the carbonyl stretching frequency, ν(CO) (in CCl_4), was noted; the observed shifts could not, however, be correlated with the corresponding Taft σ* values[7] of the substituent groups. There was no indication of split bands of the type encountered in the *ortho*-substituted benzoate

TABLE 1.

Carbonyl absorptions of some *ortho*-substituted phenylbenzoates (II) in CCl_4.

R	ν(CO)	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}
H	1746	13	665
Me	1746 *	14	690
Cl	1753	14	730
Br	1751	11	760
OMe	1748	14	655
NO_2	1756	14	720

~1·5mM-solutions in 5 mm. cells.

* Asymmetric peak.

TABLE 2.

Carbonyl absorptions of guaiacol benzoate (II; R = OMe) in various solvents.

Solvent	ν(CO)	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}
n-C_6H_{14}	1754	10	820
CCl_4	1748	14	655
$CHCl_3$	(1740 *)	26	430
$CH_3{\cdot}CN$	1740 *	17	530

~30 mM-solutions in 0·51 mm. cells, except for n-hexane (15 mM-solution in 0·51 mm. cell). Values in parentheses are approximate.

* Asymmetric peak.

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[3] Olcott, *J. Amer. Chem. Soc.*, 1937, **59**, 392.

[4] Witt and Mayer, *Ber.*, 1893, **26**, 1076.

[5] Loudon, Robertson, Watson, and Aiton, *J.*, 1950, 55.

[6] Shrewsbury, *Unicam Spectrovision*, 1958, **6**, 1.

[7] Taft, *J. Amer. Chem. Soc.*, 1953, **75**, 4231.

series, where they have been attributed to conformational isomers (IVA, IVB).[8] One compound, guaiacol benzoate (II; R = OMe), was examined in several solvents and the carbonyl absorption (Table 2) showed the expected [8] fall with increasing solvent polarity. In chloroform there was evidence of slight splitting which could be explained in terms of the existence of more than one conformation of the ester molecule or, more precisely, of its solvated complex with chloroform molecules.

(IVA) (IVB)

In contrast to the above results, two distinct carbonyl bands were observed with the introduction of a hydroxyl group into the *ortho*-position of a phenyl ester. The results for compounds of this type (I) are listed in Table 3, and illustrated in Fig. 1. At low concentrations in carbon tetrachloride where any intermolecular associations, other than with the solvent molecules, have been eliminated, the effect is concentration-independent and is readily explicable in terms of two intramolecularly hydrogen-bonded species (*e.g.*, Ia and b). Species (Ia), for which the carbonyl absorption is slightly displaced to a higher frequency relative to those of the reference compounds (Table 1; II, R = H and OMe), is analogous to that suggested by Henbest and Lovell [9] in a study of the acetates of *cis*-3,5-dihydroxy-steroids, and to the five-membered hydrogen-bonded conformation of pyrocatechol [10] and of other pyrocatechol derivatives discussed below. Species (Ib)

TABLE 3.

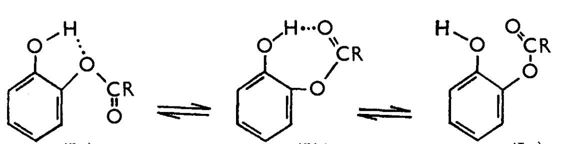
Hydroxyl and carbonyl absorptions of some *ortho*-hydroxyphenyl esters (I) in CCl_4.

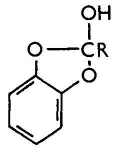
Compound (I)	R^1	R^2	ν(OH)	$\Delta\nu_{\frac{1}{2}}^a$	ε^a	ν(CO)	$\Delta\nu_{\frac{1}{2}}^a$	ε^a
O-Benzoylpyrocatechol	Ph	H	3607	sh	—	1753	17	460
			3590 *	24	85	1712 *	22	165
			(3380)	(240)	25			
O-Acetylpyrocatechol †	Me	H	3606	sh	—	1778	20	240
			3585 *	23	95	1736	16	230
			(3410)	(220)	25			
Me 3-*O*-benzoyl protocatechuate ‡	Ph	CO_2Me	3598	sh	—	1755 *	15	m
			3577 *	25	m	1726 *	15	s
			(3350)	(290)	w	1712	sh	—

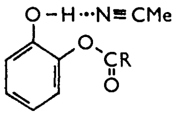
* Asymmetric peak. Cell paths for the hydroxyl and carbonyl region are 5 cm. and 2 cm., respectively, and solutions were ~0·3 mM. Measurements were made at several molarities and the absorptions above found to be concentration-independent.

† Ph acetate: ν(CO) (in CCl_4) 1768 * cm.$^{-1}$, $\Delta\nu_{\frac{1}{2}}^a$ 13 cm.$^{-1}$, ε^a 560 l. mole^{-1} cm.$^{-1}$.

‡ Me benzoate: ν(CO) (in CCl_4) 1730 cm.$^{-1}$, $\Delta\nu_{\frac{1}{2}}^a$ 11 cm.$^{-1}$, and ε^a 900 l. mole^{-1} cm.$^{-1}$. For other symbols see Tables 1 and 2.







	(Ia)	(Ib)	(Ic)	(Id)	(Ie)
ν(OH)	3590	3380	~3607	3600(?)	3365 cm.$^{-1}$
ν(CO)	1753	1712	~1750		1745 cm.$^{-1}$

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[8] Brooks, Eglinton, and Morman, *J.*, 1961, 106, 661.

[9] Henbest and Lovell, *J.*, 1957, 1965; cf. Bruice and Fife, *J. Amer. Chem. Soc.*, 1962, **84**, 1973.

[10] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.

exemplifies the seven-membered-ring type of intramolecular hydrogen bond: carbonyl and hydroxyl absorptions are both markedly lowered but the breadth of the latter suggests considerable molecular flexibility. The ester grouping cannot be planar in this conformation. The shoulder at ~3607 cm.$^{-1}$ indicates the presence of a small proportion of a conformation bearing a free hydroxyl group, for example (Ic), though species (Id) would also explain this absorption.

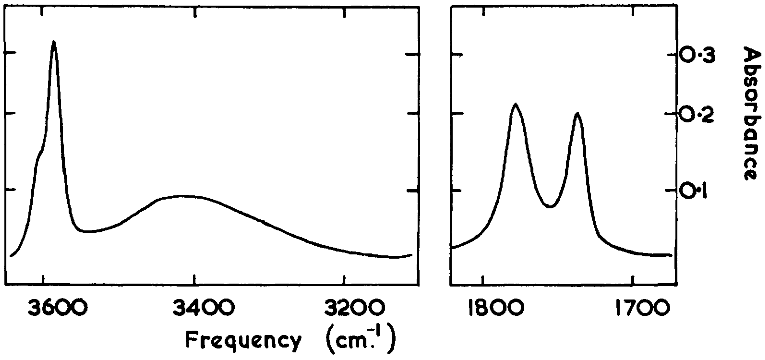


FIG. 1. Hydroxyl and carbonyl stretching absorptions of *O*-acetylpyrocatechol (I; R^1 = Me, R^2 = H) in carbon tetrachloride solution (1·65 mM) examined in 2 cm. and 0·5 cm. cells, respectively.

Similar conclusions can be drawn for the other two compounds shown in Table 3. For the protocatechuate derivative (I; R^1 = Ph, R^2 = CO_2Me) the methoxycarbonyl

TABLE 4.

Hydroxyl and carbonyl absorptions of *O*-benzoylpyrocatechol (I; R^1 = Ph, R^2 = H) in C_2Cl_4 at various temperatures.

Temp.	ν(OH)	$\Delta\nu_{\frac{1}{2}}{}^a$	ε^a	*R*	ν(CO)	$\Delta\nu_{\frac{1}{2}}{}^a$	ε^a	*R*
26°	3606	sh	—		1754	14	470	2·6
	3587	23	60	3·0	1711 *	19	180	
	(3395)	(235)	20					
50	3604	sh	—		1754	14	435	2·7
	3587	23	60	4·0	1712 *	20	160	
	(3385)	(235)	15					
80	3611	sh	—		1754	14	405	3·1
	3589	23	55	5·5	1713 *	20	130	
	(3385)	(250)	10					

Hydroxyl frequencies determined for *ca.* 10mM-solutions in 3 mm. cells. Carbonyl frequencies determined for *ca.* 5 mM-solutions in 3 mm. cells. *R* = ε^a (high-frequency band)/ε^a (low-frequency band). For symbols see Tables 1—3.

TABLE 5.

Hydroxyl and carbonyl absorptions of 1-*O*-benzoylpyrocatechol (I; R^1 = Ph, R^2 = H) in various solvents.

Solvent	ν(OH)	$\Delta\nu_{\frac{1}{2}}{}^a$	ε^a	ν(CO)	$\Delta\nu_{\frac{1}{2}}{}^a$	ε^a
n-C_6H_{14}	—	—	—	1757	11	s
				1715 *	14	w
CCl_4	3607	sh	—	1753	17	460
	3590	24	85	1712 *	22	165
	(3380)	(240)	25			
$CHCl_3$	3583 *	37	65	1746 *	22	385
	(3420)	(245)	10	1710 *	(30)	100
CH_3·CN	3365 *	(180)	105	1745	21	515

Solutions *ca.* 25 mM, except for n-hexane (saturated solution), in 0·5 mm. cell. For symbols see Tables 1—3.

group accounts for a part of the carbonyl absorption at 1726 cm.$^{-1}$. There is a higher proportion of the lower-frequency carbonyl band in the *O*-acetate (I; R^1 = Me, R^2 = H): this might be ascribed to the greater basicity of the acetate than of the benzoate carbonyl, though the changed proportions do not seem to be reflected in the hydroxyl region.

These assignments are supported by measurements for the benzoate (I; R^1 = Ph, R^2 = H) at different temperatures (Table 4) and in solvents of varying polarity (Table 5). In tetrachloroethylene increase in temperature results in the expected increase in the ratio (*R*) of the intensities of the high-frequency bands [already ascribed to the less strongly bonded form (Ia)] to the low-frequency bands. The solvent shifts for the carbonyl group showed a rough parallel with those of the model compounds (Table 2) except for the

TABLE 6.

Hydroxyl absorptions of guaiacol and related compounds (III) in CCl_4 (~1·5mM-solutions in 2-cm. cells).

Compound	ν(OH)	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}	Assignments
Va—c	3561	28	30	Intra OH · · O
	3531	56	20	Intra OH · · π
	3274	208	135	Intra OH · · O=C
o-HO·C_6H_4·O·C_6H_4·CH_2Ph-*o*	3559 *	26	120	Intra OH · · O
	3516 *	32	85	Intra OH · · π
III; R = Ph	3562	22	180	Intra OH · · O
III; R = Me	3558	24	185	Intra OH · · O

TABLE 7.

Hydroxyl absorptions of 2-*o*-hydroxyphenoxybenzophenone (V) and phenol in various solvents.

	2-*o*-Hydroxyphenoxybenzophenone				Phenol			
Solvent	ν(OH)	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}	$\Delta\nu$	ν(OH)	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}	$\Delta\nu$
n-C_6H_{14}	3570	—	w		3621	14	—	0
	3538	—	s					
	3286 *	145	s	0				
CCl_4	3561 *	28	30		3612	17	205	9
	3531 *	56	20					
	3274 *	208	135	12				
$CHCl_3$	3552 *	36	40		3599	32	150	22
	3240 *	250	100	46				
CH_3·CN	3364 *	160	115	−78	3413	140	175	208

Concentrations and cell thicknesses: for 2-*o*-hydroxyphenoxybenzophenone in n-C_6H_{14} saturated, 0·5 mm., in CCl_4 1·6 mM, 20 mm., in $CHCl_3$ 20 mM, 2 mm., and in CH_3·CN 20 mM, 0·5 mm.; for phenol in n-C_6H_{14} saturated, 0·5 mm., in CCl_4 5mM, 5 mm., in $CHCl_3$ 50 mM, 0·5 mm., and in CH_3·CN 50 mM, 0·5 mm.

Solvent shift values, $\Delta\nu = \nu$(hexane) $-$ ν(solvent) in cm.$^{-1}$. For symbols see Tables 1—3.

TABLE 8.

Carbonyl absorptions of 2-*o*-hydroxyphenoxybenzophenone (V) and benzophenone in various solvents.

	2-*o*-Hydroxyphenoxybenzophenone (V)				Benzophenone			
Solvent	ν(CO)	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}	$\Delta\nu$	ν(CO)	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}	$\Delta\nu$
n-C_6H_{14}	1670	sh	—	0	1671	8	695	0
	1660	9	—	0				
CCl_4	1667	sh	—	3	1666	10	595	5
	1657	11	690	3				
$CHCl_3$	—	sh	—	—	1658	18	490	13
	1651 *	18	500	9				
CH_3·CN	1667 *	19	300	3	1661	10	550	10
	1650 *	14	250	10				

Concentrations and cell thicknesses: for 2-*o*-hydroxyphenoxybenzophenone in n-C_6H_{14} saturated, 0·5 mm., in CCl_4 1·6 mM, 5 mm., in $CHCl_3$, 20 mM, 0·5 mm., and in CH_3·CN, 20 mM, 0·5 mm.; for benzophenone in n-C_6H_{14} 10 mM, 0·5 mm., in CCl_4 1 mM, 5 mm., in $CHCl_3$ 12 mM, 0·5 mm., and in CH_3·CN 20 mM, 0·5 mm. For symbols see Tables 1—3.

behaviour in acetonitrile where the intermolecularly bonded species (Ie) undoubtedly predominates (cf. the solvent shifts for benzophenone and phenol listed in Tables 8 and 7, respectively, and the ensuing discussion). The intramolecularly bonded species (Ia and Ib) persist in chloroform solution and it may be noted, in accordance with other experience,[8] that the solvent shift of the intrabonded carbonyl (that of Ib) is relatively small.

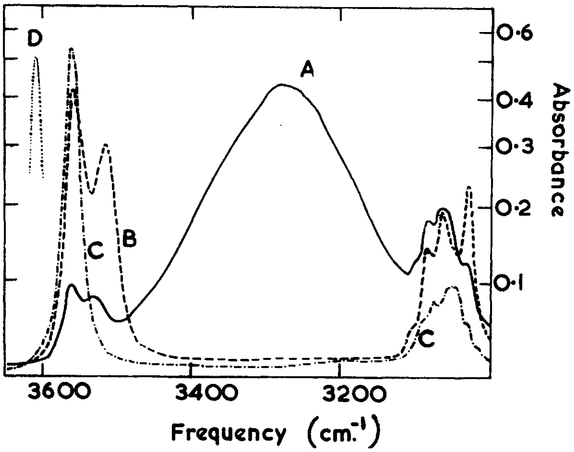


FIG. 2. Hydroxyl stretching absorptions of phenol and of certain derivatives of pyrocatechol in carbon tetrachloride.

(A) 2-*o*-Hydroxyphenoxybenzophenone (V); (B) *o*-(*o*-benzylphenoxy) phenol; (C) *o*-phenoxyphenol; and (D) phenol. Solutions (*ca.* 1·5 mM) examined in 2 cm. cell.

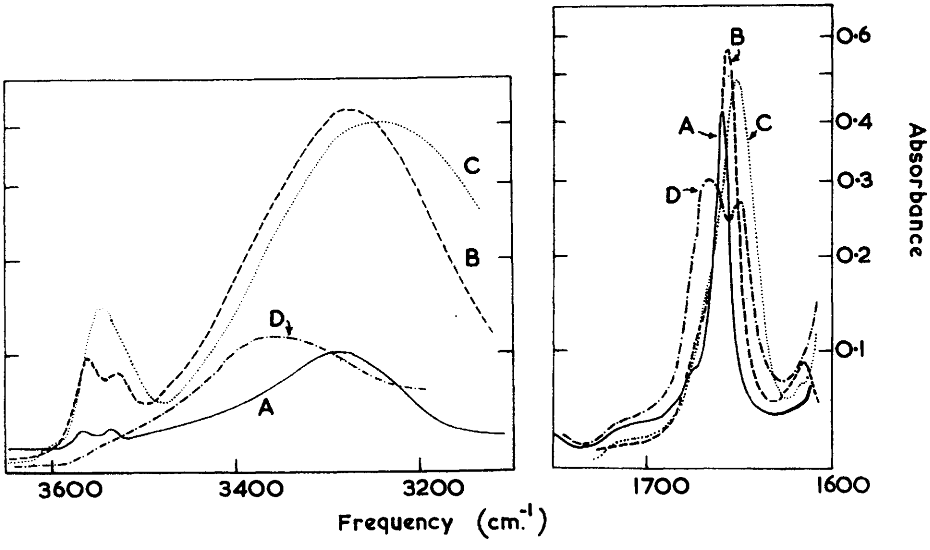
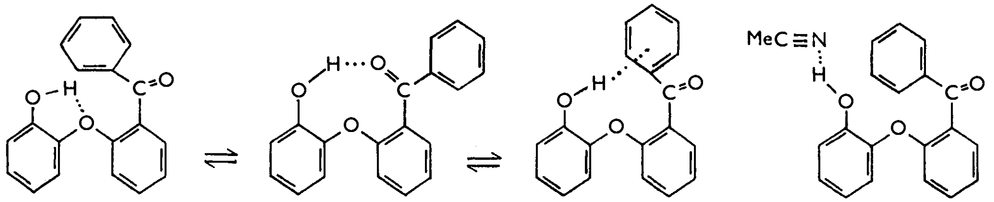


FIG. 3. Hydroxyl and carbonyl stretching absorptions of 2-*o*-hydroxyphenoxybenzophenone (V) in various solvents.

(A) n-Hexane; (B) carbon tetrachloride; (C) chloroform; and (D) acetonitrile. Concentrations and cell thicknesses are given in Tables 7 and 8.

Results for some related compounds of type (III) are given in Tables 6—8 and illustrated in Figs. 2 and 3. 2-*o*-Hydroxyphenoxybenzophenone is of special interest as here there are at least three, and possibly four, electron-rich sites for intramolecular bonding by the phenolic hydroxyl group. The absorptions have been assigned to the three conformations (V; a, b, and c) by comparison with the results in Fig. 2 and Table 6, and in the literature.[11] The conformations (Va and b) are analogous to (Ia and b), though the predominant one, (Vb), involves a hydrogen bond closing a 9-membered rather than a 7-membered ring. It is often assumed that intramolecular hydrogen bonding closes only 5- or 6-membered rings; such bonding is certainly common but there can be little doubt that formal ring size is not the most important criterion for successful intramolecular hydrogen bonding. The molecule must be free to adopt a conformation in which the hydroxyl group and the basic centre are favourably placed with respect to both distance and orientation from one another. The proportion of molecules in this form will, of course, depend on many factors, for example, the number of alternative conformations and their energy content, the nature of the solvent, and the temperature of the solution. Systems involving relatively rigid units such as the benzene ring are often fairly restricted as to the number of distinct conformations they can adopt. In such cases, conformers (*e.g.*, Vb) may be detectable which involve intramolecular hydrogen bonds between centres at first sight widely separated.[12]



	(Va)	(Vb)	(Vc)	(Vd)
ν(OH) ...	3561	3274	3531	3364 cm.$^{-1}$
ν(CO) ...	~1670	1657	~1670	1667 cm.$^{-1}$

The behaviour (Fig. 3 and Tables 7 and 8) of compound (V) in various solvents is much like that already described for the benzoate (I; R^1 = Ph, R^2 = H). The intramolecular hydrogen bonds are broken (only partially with V) in acetonitrile, but not in chloroform, as can be seen from the comparative values provided for phenol and benzophenone. The carbonyl band of 2-*o*-hydroxyphenoxybenzophenone (V) at 1650 cm.$^{-1}$ (in acetonitrile) is assigned to the intra-bonded conformer (Vb) in equilibrium with (Vd).

The conformational equilibria revealed in the present work must play some part in determining the reactivity of the compounds concerned. It is particularly interesting that the infrared method permits some evaluation, admittedly very qualitative, of the change in the proportions of the various conformers with change of solvent and of temperature. Further studies with a greater variety of substances and solvents would be of value; thus measurements in methanolic solution should show the effect of solvent on the carbonyl absorption of *o*-hydroxy-depsides of type (I) and lead to an understanding of the easy methanolysis.

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[11] Pimentel and McClellan, " The Hydrogen Bond," Freeman, San Francisco, 1960.
[12] Cairns and Eglinton, *Nature*, 1962, **196**, 535.