

985. Spectroscopic Studies of Phenols. Part II.¹ The Free Hydroxy Stretching Frequencies.

By N. A. PUTTNAM.

Further evidence is presented to show that in all phenols the hydroxyl group is coplanar with the aromatic ring and that in *ortho*-substituted phenols the hydroxyl group exists in *cis*- and *trans*-orientations with respect to the *ortho*-position. When the *ortho*-substituent is likely to take part in intramolecular hydrogen bonding the stretching frequency of the *trans*-hydroxyl group can be related to the substituent constant, as in other phenols.

IN Part I¹ the effect of substituents on the formation of intermolecular hydrogen bonding in phenols in the liquid state was described. Since it is now well established that the spectral characteristics of vibrational bands of functional groups attached to an aromatic ring are systematically influenced by the position and nature of other substituents within the ring, the small variations of the free hydroxyl stretching frequencies were not unexpected.

Thompson and Steel² have shown that the frequency and intensity of the cyano-group stretching vibration in *meta*- and *para*-substituted benzonitriles were essentially linear functions of the Hammett constant σ of the substituent, and that the relations held for different solvents. Similar relations have been established for the pair of amino-group stretching vibrations of *meta*- and *para*-substituted anilines, in both the fundamental³ and the overtone regions,⁴ for the imino-group stretching vibration in substituted *N*-methyl-anilines,³ and for the carbonyl-group stretching vibration in *meta*- and *para*-substituted ethyl benzoates, benzaldehydes, and acetophenones.⁵

It had earlier been shown by Ingraham *et al.*⁶ that the hydroxyl stretching frequencies of *meta*- and *para*-substituted phenols could be correlated to the Hammett constant σ when hydrogen bonding was absent. A similar relation was shown to exist for the intensities of these vibrations by Brown⁷ and Stone and Thompson,⁸ where it was found that the intensity increased as the electron-attracting power of the substituent increased.

Lately, these correlations have been refined⁹ by splitting the substituent constants into their inductive and resonance contributions; plotting log (intensity) or frequency against the inductive parameter σ_I for *meta*-substituents gave a straight line, and if the deviations of *para*-substituents from this line were then plotted against the resonance parameter σ_R another straight line was obtained.

Krueger and Thompson,⁹ using Taft's values¹⁰ for *ortho*-substituents, recently showed that these relations held for the cyano-group stretching vibration of *ortho*-substituted benzonitriles, but that no such agreement existed for either the carbonyl-group stretching vibration in *ortho*-substituted ethyl benzoates and benzaldehydes or for the pair of amino-group stretching vibrations in *ortho*-substituted anilines; this was considered to be due to intramolecular hydrogen-bond formation. In the case of *ortho*-substituted phenols the results agreed with those for *meta*- and *para*-substituents except when the *ortho*-substituent was likely to take part in intramolecular hydrogen bonding.

The evidence presented in the present paper shows that such phenols do agree with these relations if the minor absorption bands, due to free hydroxyl groups, are considered

Part I, *J.*, 1960, 486.

² Thompson and Steel, *Trans. Faraday Soc.*, 1956, **52**, 1451.

³ Krueger and Thompson, *Proc. Roy. Soc.*, 1957, *A*, **243**, 143.

⁴ Whetsel, Roberson, and Krell, *Analyt. Chem.*, 1958, **30**, 1598.

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

⁶ Ingraham, Corse, Bailey, and Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297.

⁷ Brown, *J. Phys. Chem.*, 1957, **61**, 820.

⁸ Stone and Thompson, *Spectrochim. Acta*, 1957, **10**, 17.

⁹ Krueger and Thompson, *Proc. Roy. Soc.*, 1959, *A*, 250, 22.

¹⁰ Taft, "Steric Effects in Organic Chemistry," Chap. 13, Wiley, New York, 1956.

rather than the major absorption bands, which arise from the intramolecular hydrogen-bonded hydroxyl vibrations; further, that in all phenols the hydroxyl group is coplanar with the aromatic ring.

Results.—The spectra were determined for CCl_4 solutions at concentrations considerably below those required for intermolecular hydrogen bonding to occur.

The hydroxyl stretching frequencies (ν) of phenols with no *ortho*-substituents are listed in

TABLE 1. *Hydroxyl stretching frequencies (cm.⁻¹) of phenols with no ortho-substituents. [Apparent half-band widths (cm.⁻¹) in parentheses.]*

Substituent	$\Sigma\sigma$	ν (O-H)	Mean lit. values	Substituent	$\Sigma\sigma$	ν (O-H)	Mean lit. values
None	0	3611 (18)	3609 \pm 1 ^a (19 \pm 2)	4-Bu ^t	-0.22	3614 (20)	3612
3-NH ₂	-0.16		3612	4-Ph	0.01		3611 \pm 1 (21)
3-NO ₂	0.71		3599 \pm 1 ^b (24)	4-MeO	-0.27		3614 \pm 2 ^f (21 \pm 1)
3-OH	0.002		3609 \pm 1	4-Ph·CH ₂ ·O	-0.41 ^g		3615 \pm 2 (19)
3-Me	-0.07		3611 ^e	4-OH	-0.36		3617 (18)
3-Et	-0.04		3611	4-F	0.06		3607
3,5-Me ₂	-0.17 ⁷	3613 (21)	3612 \pm 1 (22)	4-Cl	0.23		3608 \pm 1 ^g (21 \pm 1)
3-CHO	0.35		3604 \pm 1 (22)	4-Br	0.23	3607 (24)	3607 \pm 1 ^h (22 \pm 1)
3-OMe	0.12		3612 ^d	4-I	0.28		3599
3-F	0.34		3600	4-CN	1.00		3594 (23)
3-Cl	0.37		3604 \pm 3 (23)	4-NO ₂	1.27		3594 \pm 1 ^j (24)
3-Br	0.39		3604 ^e (23)	4-CHO	1.13		3594 \pm 2 (22)
4-Me	-0.17		3612 \pm 1 (18 \pm 1)	4-NH ₂	-0.66		3613 \pm 1
3,4-Me	-0.30 ⁸	3615 (19)	3613 \pm 2 (19 \pm 1)	4-CO ₂ Et	0.68		3595
4-Pr ⁱ	-0.15	3616 (18)		4-CO ₂ Me	0.64		3594
4-Bu ⁿ	-0.16	3617 (18)		4-Cl, 3-Me	0.16	3608 (22)	
4-Bu ^o	-0.12	3615 (19)		4-Pr ⁱ , 3-Me	-0.22	3616 (18) [*]	

* Saturated solution.

Ref. 12 gives: ^a 3604, ^b 3593, ^c 3605, ^d 3604, ^e 3597, ^f 3609, ^g 3602, ^h 3600, 3585 cm.⁻¹.

TABLE 2. *Hydroxyl stretching frequencies (cm.⁻¹) of phenols with one ortho-substituent. [Apparent half-band widths (cm.⁻¹) in parentheses.]*

Substituent	$\Sigma\sigma$ [*]	ν (O-H)	Mean lit. values	Substituent	$\Sigma\sigma$ [*]	ν (O-H)	Mean lit. values
2-Me	-0.17	3615 (21)	3614 (21.5)	4-Me, 2,5-Bu ^t ₂			3606
2,3-Me ₂	-0.24		3615 (21.5)				3642
2,4-Me ₂	-0.34	3617 (22)	3616 (21)	4-Me, 2-Bu ^t		3609 (19)	3605
2,5-Me ₂	-0.24	3614 (22)	3614 (21)			3645 (—)	3643
2,3,5-Me ₃	-0.31	3617 (22)		2-F	0.24		3584
2-Pr ⁱ			3615 \pm 1 (21.5)	2-Cl	0.20		3546 \pm 4 (22 \pm 1)
4-Et, 2-Pr ⁱ		3617 (19)					3605 \pm 6 (—)
3-Me, 2Pr ⁱ		3616 (19)		2,4-Cl ₂	0.43	3544 (23)	
		3642 (—)				3604 (—)	
4-Me, 2-Bu ^o		3617 (20)		2-Br	0.21	3527 (22)	3526 \pm 2 (21)
2,4-Bu ^o ₂		3616 (21)				3608 (—)	3602 \pm 3 (—)
2-I	0.21		3500	2,4-Br ₂	0.44	3523 (22)	
			3593			3603 (—)	
2-Ph			3562 \pm 3 (19.5)	2-OEt	-0.35		3555 (27)
			3604 \pm 1 (—)				3613 (—)
2-OMe	-0.39		3555 \pm 2 (26)	2-OMe, 4-CHO	0.74		3542 (25)
2-OH	-0.10 ⁹		3569 (27)	2-OMe, 4-CN	0.61		3549 (24)
			3615 (26.5)				
2-CN	0.64 ⁹		3559 (23)				
			3597 \pm 2 (—)				

* Involving Taft's *ortho*-constant.

Table 1, together with the mean literature values.^{8-9,11-13} Also listed are the apparent half-band widths ($\Delta\nu_{1/2}$) and the Hammett constant $\Sigma\sigma$ ¹⁴ of the substituent ($\Sigma\sigma$ when more than one substituent is present). These phenols showed only one absorption band in this region.

¹¹ Goulden, *Spectrochim. Acta*, 1953, **6**, 129.

¹² Baker, *J. Phys. Chem.*, 1958, **62**, 744.

¹³ Moccia and Thompson, *Proc. Roy. Soc.*, 1957, *A*, **243**, 154.

¹⁴ Jaffe, *Chem. Rev.*, 1953, **53**, 191.

Similar data for phenols with one *ortho*-substituent are listed in Table 2.^{9,15-19} The *o*-alkylphenols showed only one absorption band in this region except 2-isopropyl-3-methyl-, 4-methyl-2-*t*-butyl-, and 4-methyl-2,5-di-*t*-butylphenol where a minor absorption band appeared on the high-frequency side of the main absorption band (Fig. 1); the apparent half-band widths of these minor absorption bands were not determined. When the *ortho*-substituent was halogen, alkoxy, phenyl, or cyano, Krueger and Thompson found that a second absorption band, not reported by Flett,¹⁵ was present except in the case of a methoxy-group. In *o*-halogenophenols Baker¹⁶ showed that this minor band was not due to the presence of the *para*-isomer as an impurity.

FIG. 1. Spectra of (A) *o*-bromophenol, (B) 2,6-dibromo-4-methylphenol, (C) 4-methyl-2-*t*-butylphenol, (D) 4-methyl-2,6-di-*t*-butylphenol.

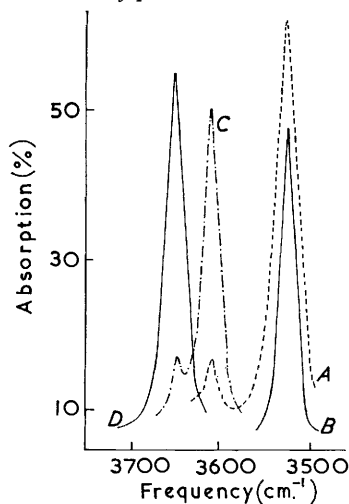


FIG. 2. Plot of hydroxyl stretching frequency (in terms of $\Delta\nu$, cm^{-1}) against total substituent constant $\Sigma\sigma$.

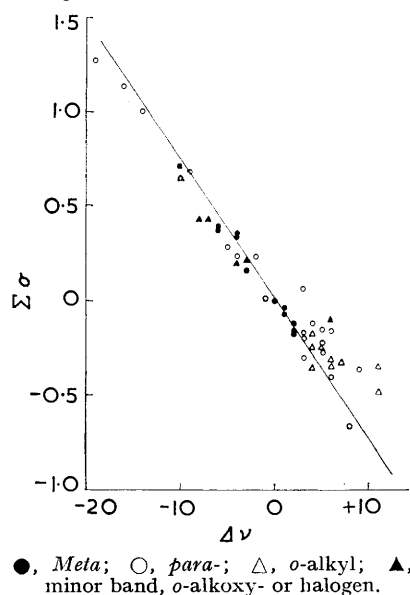


TABLE 3. Hydroxyl stretching frequencies (cm^{-1}) of di-*ortho*-substituted phenols. [Apparent half-band widths (cm^{-1}) in parentheses.]

Substituent	$\Sigma\sigma^*$	ν (O-H)	Mean lit. values	Substituent	$\Sigma\sigma^*$	ν (O-H)	Mean lit. values
2,6-Me ₂	-0.34		3621 ± 1 (20)	2,6-Et ₂			3622
2,3,5,6-Me ₄	-0.48	3622 (23)		2,6-Pr ₂			3618 ± 2
2,6-Pr ₂ , 4-Me		3623 (20)		4-Me, 2,6-Bu ^s ₂		3623 (20)	
2,6-Bu ^s ₂		3620 (19)		2,4,6-Bu ^s ₃		3620 (22)	
2,6-Bu ^t ₂		3651 (16)	3642	4-Me, 2,6-Bu ^t ₂		3649 (17)	3648 ± 2
2,4,6-Bu ^t ₃			3642	2,6-(OMe) ₂	-0.78		3548
2,6-Cl ₂	0.40	3538 (23)		2,4,6-Cl ₃	0.63		3537 (22.5)
2,3,4,6-Cl ₄	1.00	3539 (23)		2,4,6-Br ₃	0.65		3515 (22.5)
2,6-Br ₂ , 4-Me	0.25	3524 (24)		2,6-Br ₂ , 4-F	0.48	3528 (22)	
2-F, 4,6-I ₂	0.73		3568	4,6-Br ₂ , 2-F	0.68	3522 (25)	3522
			3504			3578 (26)	3574
2-F, 4,6-Cl ₂	0.67		3541	4,6-Cl ₂ , 2-I	0.64		3535
			3580				3502
2-Br, 4,6-Cl ₂	0.64		3535	4,6-Br ₂ , 2-I	0.65		3515
			3515				3496

* Involving Taft's *ortho*-constant.

¹⁵ Flett, *Spectrochim. Acta*, 1957, **10**, 21.

¹⁶ Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 3598.

¹⁷ Goddu, *Analyt. Chem.*, 1958, **30**, 2009.

¹⁸ Bellamy and Williams, *Proc. Roy. Soc.*, 1960, **A**, 254, 119.

¹⁹ Baker and Shulgin, *J. Amer. Chem. Soc.*, 1958, **80**, 5358.

This second band was relatively weak and occurred on the higher-frequency side of the main absorption band (Fig. 1); with catechol, however, the two bands were of almost equal intensity.⁹

Table 3 records the data for phenols with substituents in both *ortho*-positions.^{9,17-20} The spectra of these phenols showed only one absorption band (Fig. 1) except in the unsymmetrical di-*o*-halogenophenols, where two absorption bands were present.

DISCUSSION

The hydroxyl stretching frequencies reported here are in agreement with those previously reported and follow the general trend, noticed by Stone and Thompson,⁸ that as the electron-attracting nature of the substituent increased the hydroxyl stretching frequency was lowered, owing to the increased positive charge on the oxygen atom. This is the reverse of that found for the pair of amino-group stretching vibrations in substituted anilines.³

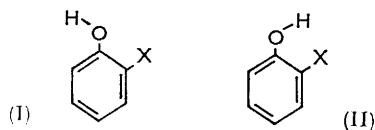
In order that the results of various workers might be compared, $\Delta\nu$ [where $\Delta\nu = \nu$ (sample) - ν (phenol)] has been plotted against $\sum\sigma$ (Fig. 2) since relative frequencies are known with greater accuracy than absolute frequencies.

The usual linear plot of ν against σ was obtained for *meta*-substituents, and for *para*-substituents the expected slight deviations, due to resonance effects, were shown, the maximum deviation being 4 cm.⁻¹ for quinol. The deviations for *o*-alkyl substituents were of the same order of magnitude as those for the *para*-substituents.

However, in the case of *ortho*-substituents that were likely to take part in intramolecular hydrogen bonding, *e.g.*, ethoxy-, cyano-, and bromo-groups, the values of $\Delta\nu$ for the major absorption band (-54, -50, and -81 cm.⁻¹, respectively) deviated very considerably, but when the values of $\Delta\nu$ for the minor absorption band were plotted, in the cases where the σ values of the *ortho*-substituent were known, the agreement was as good as that obtained for *p*- and *o*-alkyl substituents; the maximum deviation being 4.5 cm.⁻¹ in the case of catechol, where the value of σ was obtained from spectroscopic data.⁹

The apparent half-band width of the hydroxyl group in 2,6-di-*t*-butylphenols was reduced, owing to compression of the hydroxyl bond (discussed below), while in other phenols it had previously been shown⁸ that it increased as the electron-attracting nature of the substituent increased.

Owing to the absence of interaction between the hydroxyl group and the hydrogen atom in the *ortho*-position in *meta*- or *para*-monosubstituted phenols, the hydroxyl group will be coplanar with the aromatic ring, thus allowing conjugation between the lone pair of electrons on the oxygen atoms and the aromatic π -cloud. From a study of the intensities of the hydroxyl-group stretching vibration in 2,6-dialkylphenols, in various solvents, Bellamy and Williams¹⁸ concluded that the hydroxyl group was in the plane of the ring, even when the alkyl group was *t*-butyl. In mono-*ortho*-substituted phenols, if the hydroxyl group is in the plane of the ring, the hydroxyl group will exist in *cis*- and *trans*-orientations with respect to the *ortho*-position, as suggested by Pauling²¹ to explain the doubling of the hydroxyl group stretching vibration in *ortho*-halogenophenols.



In structure (I) the hydroxyl group would be subjected solely to the resonance and inductive effects of the substituent X, as in *meta*- and *para*-substituted phenols, and would be expected to show a similar relationship between ν and σ to that shown in *meta*- and *para*-substituted phenols. This was found to be true when X was a methyl group.⁹

²⁰ Baker and Kaeding, *J. Amer. Chem. Soc.*, 1959, **81**, 5904.

²¹ Pauling, *J. Amer. Chem. Soc.*, 1936, **58**, 94.

From Fig. 2 it is seen that it is also true for an *ortho*-substituent that will take part in intramolecular hydrogen bonding, *i.e.*, X = OEt, CN, or halogen, when the minor absorption band is considered. Hence this band arises from vibrations of a hydroxyl group in a *trans*-orientation (I).

In 2,6-disubstituted phenols structures (I) and (II) would be equivalent and only one absorption band would be expected, corresponding to structure (II); this was found to be so.

For phenols with two *ortho*-substituents, which would take part in intramolecular hydrogen bonding (X = Cl or Br), the value of $\Delta\nu$ is essentially the same as that of the major absorption band of similar mono-*ortho*-substituted phenols. Hence the major absorption band arises from vibrations of an hydroxyl group in a *cis*-orientation (II).

In structure (II) the probability of interaction is greatly increased, with the result that hydrogen bonds of low strength are formed, which accounts for only a slight increase in the apparent half-band width of the hydroxyl stretching vibration and the small shift from the hydroxyl stretching frequency of phenol relatively to that usually found for intramolecular hydrogen-bond formation.²² The fact that iodine appears to form a stronger intramolecular hydrogen bond than fluorine has been attributed by Baker and Kaeding²⁰ to the smaller size of the latter. The fact that the minor absorption band was not detected when the *ortho*-substituent was a fluoro-¹⁶ or a methoxy-group⁹ in mono-*ortho*-substituted phenols was probably due to the low intensities of these bands.

Two absorption bands were also detected when the *ortho*-substituent in mono-*ortho*-substituted phenols was *t*-butyl. The major band occurred at a similar frequency to that shown by other *o*-alkylphenols and could probably be related to the substituent constant. The minor absorption band occurred at essentially the same frequency as that for 2,6-di-*t*-butylphenols, where the *cis*-orientation must exist, and hence must arise from vibrations of a hydroxyl group in the *cis*-orientation.

A *t*-butyl group in the *ortho*-position to the hydroxyl group reduced the hydroxyl internuclear distance, resulting in the hydroxyl stretching frequency being raised. Other alkyl groups in the *ortho*-position are not large enough to increase the hydroxyl stretching frequency and hence only one absorption band was detected. Similarly, in unsymmetrical 2,6-dialkylphenols only one absorption band was detected so that the *cis*- and *trans*-orientation are equivalent; however, in 2-methyl-6-*t*-butylphenol two absorption bands would be expected. These results were in agreement with earlier results¹ where it was shown that intermolecular hydrogen bonding occurred in all *o*-alkylphenols except when the alkyl group was *t*-butyl. The occurrence of two bands in 2-isopropyl-3-methylphenol was due to the buttressing effect of the 3-methyl group on the isopropyl group.

It is concluded that all phenols exist with the hydroxyl group coplanar with the ring and in a *cis*- and *trans*-orientation with respect to the *ortho*-position. If an *ortho*-substituent will take part in intramolecular hydrogen bonding, *e.g.*, phenyl, alkoxy, cyano, or halogen, then the hydroxyl group is mainly in the *cis*-orientation, but if it is a *t*-butyl group it is mainly in the *trans*-orientation.

Several workers have determined substituent constants from spectroscopic data;^{9,23} from Fig. 2 it is possible to obtain an approximate σ value for an *ortho*-*s*-butyl group of -0.25 .

Experimental.—The phenols examined were purified by fractional distillation or recrystallisation immediately before examination. Spectra were measured on a Grubb-Parsons G.S.2A double-beam grating spectrometer over the range 4000—3000 cm^{-1} . Hydroxyl stretching frequencies were determined for "AnalaR" CCl_4 solutions ($<7 \times 10^{-3}\text{M}$), with a 4.1 mm. cell.

The author thanks Professor M. J. S. Dewar for facilities, Mr. P. D. Cook for experimental assistance, and Mr. P. Marr for the samples of 2,6-dibromo-4-fluoro- and 2,4-dibromo-6-fluorophenol.

QUEEN MARY COLLEGE (UNIVERSITY OF LONDON), MILE END ROAD,
LONDON, E.1.

[Received, April 20th, 1960.]

²² Coggeshall, *J. Amer. Chem. Soc.*, 1950, **72**, 2836.

²³ Baker and Shulgin, *J. Amer. Chem. Soc.*, 1959, **81**, 1523.