Experimental Observations and CNDO/2 Calculations for Hydroxy Stretching Frequency Shifts, Intensities, and Hydrogen Bond Energies of Intramolecular Hydrogen Bonds in *ortho*-Substituted Phenols

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I.r. spectral measurements were made to obtain frequency shifts ($\triangle\nu_{OH}$) and integrated intensities (A_{OH}) of the hydroxy stretching vibration for intramolecular hydrogen bonding in *ortho*-substituted phenols in dilute carbon tetrachloride solution. ^{1}H N.m.r. spectra were also measured to observe the chemical shift of the hydroxy proton. Two kinds of correlations were found between $\triangle\nu_{OH}$ and A_{OH}: one was a large increase of A_{OH} with increasing $\triangle\nu_{OH}$, and the other a small increase of A_{OH}. The former was found in phenols having a proton acceptor unconjugated with the benzene ring and the latter in those having a conjugated acceptor. The latter correlation was interpreted as resulting from a large delocalization effect of the OH bond electrons through the hydrogen bond system; this was supported by model calculations using the CNDO/2 method to estimate A_{OH}. A linear correlation was also found between $\triangle\nu_{OH}$ and $\triangle\delta_{OH}$. An empirical equation linearly relating the hydrogen bond energy to $\triangle\nu_{OH}$ is proposed. The calculated force constants, frequency shifts, and energies for the hydrogen bond systems were compared with the experimental data giving a fairly good result.

THE phenomenon of hydrogen bonding is of fundamental importance in physical chemistry and biology. Many i.r. studies of inter-[1-4] and intra-molecular[5-11] hydrogen bonding of the phenolic hydroxy group have been reported. In general, the stronger the hydrogen bond, the greater the magnitudes of the OH stretching frequency shift ($\Delta\nu_{OH}$) and the integrated intensity (A_{OH}).[1-3,12,13] The size of $\Delta\nu_{OH}$ or A_{OH} found in phenols is almost twice that for aliphatic hydroxy groups.[1,2] Many relationships between $\Delta\nu_{OH}$ or A_{OH} and various physicochemical properties have been reported.[2-4,7,13-25] However, only a few studies on the nature of A_{OH} have been reported.[1,2,7,12,16] We have extensively studied hydrogen bonding systems to clarify the relation of $\Delta\nu_{OH}$ to A_{OH}. Recently,[4] a linear relationship was demonstrated between the calorimetrically determined enthalpy ($-\Delta H$) and the change in frequency of the OH stretching vibration of the intermolecular hydrogen bond in substituted phenols. The equation is $-\Delta H = 0.010\,3\Delta\nu_{OH} + 3.08$. On the other hand, a similar equation for intramolecular hydrogen bonding in *ortho*-substituted phenols cannot be readily established usually due to the presence of one overwhelmingly predominant form in the equilibrium. Schaefer[23] has related intramolecular hydrogen bond energies (E) to ^{1}H chemical shifts of the hydroxy proton as well as to OH torsional frequencies (ω_t) and has suggested the linear equation $\Delta\delta_{OH}$ (or $0.017\Delta\omega_t$) $= -0.4 + E$.

Reeves *et al.*[20] have proposed a linear relationship between OH stretching frequency shifts and ^{1}H chemical shifts of hydroxy protons in *ortho*-substituted phenols. Nyquist[21] has found a correlation between OH stretching frequencies and OH torsional frequencies in the same system. Their studies lead us to expect a linear relationship between intramolecular hydrogen bond energies and OH stretching frequency shifts in *ortho*-substituted phenols. Here we report an empirical linear equation for the above relationship. Molecular orbital calculations have been applied to a variety of hydrogen bonding systems,[25-31] but not to the problems of the OH stretching force constant and the integrated intensity of the intramolecular hydrogen bonding system, except for one paper.[26] Therefore, we carried out CNDO/2 calculations for some model systems of *ortho*-substituted phenols to obtain an approximate value of the OH stretching shifts, dipole moment derivatives, and hydrogen bond energies. The theoretical predictions could be well correlated with the experimental results.

EXPERIMENTAL

The compounds used were obtained commercially or synthesized in our laboratory.† They were purified by standard methods until their physical constants agreed well with the published values. I.r. measurements were carried out using a JASCO DS-402G grating spectrometer calibrated in the usual manner. Samples were dissolved in purified CCl$_4$ (redistilled and stored over P$_2$O$_6$) at a concentration (c) below 0.005M (cell length $l = 1$ or 2 cm), so that self-association of the OH groups was excluded. Ramsay's method[32] was used to calculate values of A_{OH}, defined by equation (1) where $\Delta\nu_{1/2}$ is the band width (cm^{-1})

$$A = (\pi/2)[\ln(I_0/I)](cl)^{-1}\Delta\nu_{1/2} \qquad (1)$$

at half intensity. The values of $\Delta\nu_{OH}$ (cm^{-1}) were obtained as the difference of the observed OH stretching frequency ν_{OH} (cm^{-1}) from that of the phenol band at 3 612 cm^{-1} ($\Delta\nu_{OH} = 3\,612 - \nu_{OH}$). The accuracy of $\Delta\nu_{OH}$ and A_{OH} for the ν_{OH} band observed at above 3 200 cm^{-1} was within ± 2 cm^{-1} and $\pm 5\%$, respectively. Because the ν_{OH} band observed below 3 200 cm^{-1} was very broad and overlapped with the CH bands, the accuracy of $\Delta\nu_{OH}$ and A_{OH} in this frequency range was worse than in the above case. All measurements were carried out at room temperature (*ca.* 27 °C).

N.m.r. spectra of the hydroxy group of *ortho*-substituted phenols were recorded on a Varian A-56/60D spectrometer operating at 60 MHz. Samples were dissolved in CDCl$_3$ at concentrations lower than 30 mg per 0.4 ml. The spectra of solutions diluted to 1/4 and 1/10 (and to 1/50 in some cases) were also measured at the same temperature, but the signals showed no change. Chemical shifts were expressed as δ_{OH}, downfield from the internal reference TMS. For 2-

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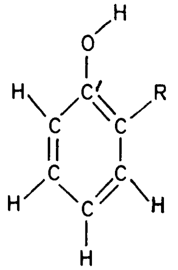
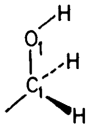
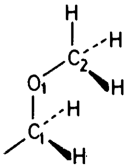
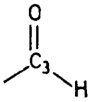
† See Table 2, footnote *e*.

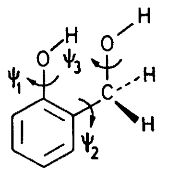
hydroxybenzyl alcohol, the spectra were also recorded in $CDCl_3$ (0.067M) at −17.0 °C and in C_6D_6 (0.1M) at 39.5 °C. The $\Delta\delta_{OH}$ values described are the difference between the observed δ_{OH} and that of phenol ($\Delta\delta_{OH} = \delta_{OH} - 4.70$ or 4.29); δ 4.70[33] and 4.29[23] are the values for phenol at infinite dilution in $CDCl_3$ and CCl_4, respectively. The accuracy of δ_{OH} for the sharp signals was within ±0.02. With the broad signals, an accuracy of *ca.* ±0.05 was accepted, because of ambiguity in designating the centre of the signal.

TABLE 1

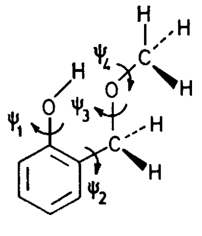
Bond lengths (Å) and angles (°)[35-37] of the molecules used in the CNDO/2 calculations

Compound		R	Geometry	
	(A)	H	R_{OH} ~0.96 $R_{C'O}$ 1.38 R_{CC} 1.395 R_{CH} 1.08	$C\widehat{O}H$ 110 $C\widehat{C}C$ 120 $C\widehat{C}H$ 120 $C\widehat{C}O$ 120
	(B)		$R_{O(1)H}$ 0.96 $R_{C(1)O(1)}$ 1.43 $R_{CC(1)}$ 1.52 $R_{C(1)H}$ 1.10 Torsion angle CC(1)O(1)H [a]	$C(1)\widehat{O}(1)H$ 109
	(C)		$R_{C(2)O(1)}$ 1.43 $R_{C(2)H}$ 1.09 Torsion angle CC(1)O(1)C(2) [a]	$C(1)\widehat{O}(1)C(2)$ 109
	(D)		$R_{C'O}$ 1.36 $R_{C(3)=O}$ 1.24 $R_{CC(3)}$ 1.46 $R_{C(3)H}$ 1.09 Torsion angle C′CC(3)O 0°	CC(3)O 120 $O\widehat{C}(3)H$ 120

[a] See text.



(B)



(C)

CALCULATIONS

The CNDO/2 calculations were carried out using the computer program of Pople and Beveridge[34] on an IBM 370/158 computer. On the basis of available electron diffraction,[35] microwave,[36] and *X*-ray[37] data on analogous compounds, we adopted the geometries of the *ortho*-substituted phenols (A)—(D) shown in Table 1. However, the geometries of (B) and (C) in which the rotation about C–C and C–O bonds may lead to two kinds of conformations, planar and non-planar forms, are not clearly defined at present. The geometry of (B) could not be determined from n.m.r. and i.r. spectra, as will be discussed later in detail. Therefore the CNDO/2 calculations were carried out by assuming both planar and non-planar forms for (B) and (C). All torsion angles for the planar form (B_1) of (B) and that (C_1) of (C) were assumed to be 0°. On the other hand, all torsion angles for the non-planar form (B_2) of (B) were estimated by minimum energy geometry using the CNDO/2 method. The calculated torsion angles for (B_2), ψ_1—ψ_3, were 10, 26, and 7°, respectively, for the most stable conformation. These values were obtained by assuming 109° 28′ for $C\widehat{C}O$ in the substituent. The actual angle may be slightly larger than 109° 28′ because of internal repulsion. If this is the case, it is anticipated that all the torsion angles calculated by the same procedure will be smaller than the above angles. When the torsion angle ψ_3 was calculated by keeping ψ_1 and $\psi_2 = 0°$, $\psi_3 = 0°$ was estimated to give the most stable conformation. In view of the similarity between (B) and (C), the torsion angles for the non-planar form (C_2) of (C) were assumed to be the same as those for (B_2). The methyl protons of (C) were placed for minimum repulsion by the methylene protons. The torsion angles ψ_4 for (C_1) and (C_2) were 0 and −7°, respectively. For the C–O bond length between the benzene ring and OH, 1.38 Å was used for (A)—(C), and 1.36 Å for (D). At first, the total energies *E* for (A) and *cis*-(B)—(D) were calculated at 0.1 Å intervals of the phenolic OH bond length (R_{OH}) from 0.76 to 1.56 Å and then at 0.01 Å intervals of R_{OH} about the energy minimum. The same procedure was applied to the CNDO/2 calculations for *trans*-(B)—(D) (at ψ_1 180°). The molecular dipole moments * were also calculated at the same time. The potential curves obtained show energy minima in the range 1.03—1.05 Å. The proton potential and dipole moment functions necessary for subsequent treatments were obtained by five-point calculations at 0.01 Å intervals of R_{OH} around the energy minimum in each case. Optimum

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* The dipole moment has the opposite direction to usual chemical convention.[34]

TABLE 2

Experimental ν_{OH} cm^{-1},[a] $\Delta\nu_{OH}$ cm^{-1},[b] 10^{-4} A_{OH} mol^{-1} l cm^{-2},[c] and δ_{OH} [d] values for intramolecular hydrogen bonds in *ortho*-substituted phenols [e]

No.	Compound	ν_{OH}	$\Delta\nu_{OH}$	$10^{-4}A_{OH}$	δ_{OH}
(1)	Phenol	3 612	0	1.15	4.70 [f]
(2)	2-Hydroxybenzyl alcohol	3 607	5	1.12	
		3 440	172	3.00 *	~7.1
(3)	2-Hydroxy-α,5-dimethylbenzyl alcohol	3 602	10	0.93	
		3 426	186	3.08 *	7.61
(4)	2-(2-Methyl-1,3-dioxolan-2-yl)-*p*-cresol	3 406	206	3.76 *	7.95
(5)	3,3′-Bis-(2-methyl-1,3-dioxolan-2-yl)-2,2′-dihydroxy-5,5′-dimethylbiphenyl	3 395	217	8.23	8.13
				(4.12) *,[g]	
(6)	3,3′,9-Triacetyljulichrome $Q_{1,3}$	3 473	39	0.09	
		3 262	350	5.96	8.70 [a]
				(6.2) *,[h]	
		~2 970	~642	3.08 *	12.50 [b]
(7)	3,10-Didemethoxy-9-demethyl-14-deoxocryptopromatine	3 612	0	0.03	
		~2 930	~682	~10.12	
				(~10.3) *,[h]	
(8)	2,10-Didemethoxy-9-demethyl-14-deoxyocryptopromatine	3 612	0	0.03	
		~2 930	~682	~10.07	
				(~10.2) *,[h]	
(9)	Cacalol	3 591	21	1.27 *	
(10)	2-Methoxyphenol [i]	3 558	54	1.61 *	
(11)	1,5-Dihydroxyphenazine	3 445	167	2.50	
				(1.25) *,[g]	
(12)	2-Methyl-8-hydroxyquinoline	3 412	200	2.26 *	7.40
(13)	1-Hydroxyfluoren-9-one	3 402	210	1.11 *	8.42
(14)	2-Nitrophenol	3 231	381	1.75 *	10.51
(15)	Methyl salicylate	3 204	408	2.83 *	10.70
(16)	Salicylaldehyde	~3 130	~482	~2.23 *	10.98
(17)	5-Hydroxy-1,4-naphthoquinone	~3 100	~512	~2.26 *	11.85
(18)	1,8-Dihydroxyanthraquinone	~3 100	~512	~4.40	11.93
				(~2.20) *,[g]	
(19)	1-Hydroxyanthraquinone	~3 020	~598	~3.40 *	12.47
(20)	4,6-Dimethylsalicylaldehyde	~3 000	~612	~2.90 *	
(21)	2-Hydroxy-5-methylacetophenone	~3 000	~612	~3.28 *	12.05
(22)	3,3′-Diacetyl-2,2′-dihydroxy-5,5′-dimethylbiphenyl	~2 960	~652	~6.79	12.45
				(~3.39) *,[g]	
(23)	2-Hydroxy-2′-methoxy-5,5′-dimethylbiphenyl	3 558	54	0.27	
		3 435	177	2.40	6.12
(24)	3-(2-Methyl-1,3-dioxolan-2-yl)-2,2′-dihydroxy-5,5′-dimethylbiphenyl	3 564	48	0.18	
		3 400	212	2.84	6.52 [a]
		3 287	325	4.09	9.10 [b]
(25)	2,2′-Dihydroxy-3-acetyl-5,5′-dimethylbiphenyl	3 574	38	0.08	
		3 420	192	3.18	6.45 [a]
		~2 900	~662	~5.05	13.35 [b]

[a] I.r. spectra were measured in CCl_4 solutions at concentrations <0.005M. [b] $\Delta\nu_{OH} = \nu_{OH}$ (1) − ν_{OH}. [c] The $10^{-4}A_{OH}$ values asterisked correspond to those for complete formation of an intramolecular hydrogen bond. [d] N.m.r. spectra were measured in $CDCl_3$ solutions at concentrations <30 mg per 0.4 ml. [e] Compounds (1), (2), and (11)—(19) were obtained commercially. Compounds (3)—(6) and (20)—(25) were supplied by N. Tsuji and K. Nagasima, (7) and (8) by S. Maeda, and (9) by K. Horibe. [f] Ref. 33. [g] The $10^{-4}A_{OH}$ values in parentheses are those for one OH group. [h] The $10^{-4}A_{OH}$ values in parentheses were estimated by extrapolation to 100% formation of the hydrogen bond. [i] Ref. 8.

bond lengths (R_{OH°) were obtained from the proton potential functions. The hydrogen bond energies were obtained as the differences ΔE between the total energies of the *cis*- and *trans*-isomers and were compared with experimental intramolecular hydrogen bond energies $-\Delta H$. The OH stretching force constants k and the dipole moment derivatives $\partial\mu/\partial R_{OH}$ were calculated from the proton potential and dipole moment functions and were compared with the experimental values obtained from i.r. measurements.

RESULTS AND DISCUSSION

(a) *Frequency Shift-Integrated Intensity Correlations.*—The values of ν_{OH}, $\Delta\nu_{OH}$, A_{OH}, and δ_{OH} observed for the *ortho*-substituted phenols are shown in Table 2. When the integrated intensities of the OH stretching vibration A_{OH} were plotted against the corresponding frequency shift $\Delta\nu_{OH}$, two linear relationships, types [I] and [II], were found, as shown in Figure 1. Type [I] shows a large increase in A_{OH} with increasing $\Delta\nu_{OH}$, while type [II] shows a small increase. From the structural viewpoint, the compounds in the type [I] relationship have a sp^3 carbon between the benzene ring and the proton acceptor X, but the compounds for the type [II] correlation do not have such a carbon-inhibiting conjugation between X and the benzene ring. Thus the delocalization between OH and X is very accentuated in compounds of type [II] but negligible for those of type [I], assuming that the effect of hyperconjugation and the inductive effect through the CH_2 group is small. According to Tsubomura,[1] the dipole moment induced by intramolecular hydrogen bonding for the OH $\cdots$ X system is decreased by delocalization of the π-electron. This is the main reason why the A_{OH} : $\Delta\nu_{OH}$ ratio of type [II] is smaller than that of type [I]. A_{OH}–$\Delta\nu_{OH}$ Relationships have been studied for intermolecular hydrogen bond systems in which the delocalization between phenol and various proton acceptors is negligible. The A_{OH} : $\Delta\nu_{OH}$

ratios observed for these systems are much larger than that for type [I]. This is probably due to the fact that in general, the O–H · · · X angles for the intramolecular hydrogen bonds are smaller than 180° but those for the intermolecular hydrogen bonds are equal or close to 180°.[24,25]

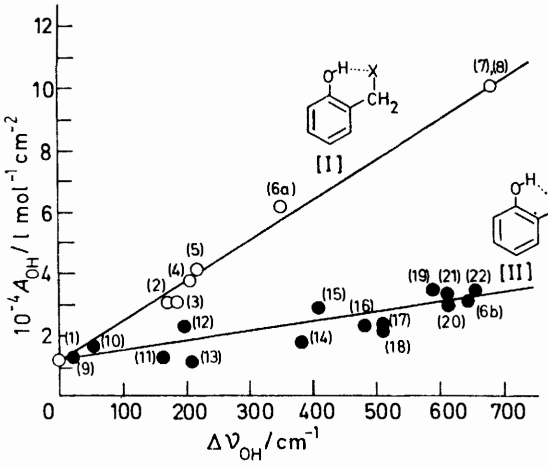


FIGURE 1 Plot of $10^{-4}A_{OH}$ against $\Delta\nu_{OH}$ for intramolecular hydrogen bonds in *ortho*-substituted phenols (for key see Table 2)

(b) *Frequency Shift–Hydrogen Bond Energy Correlation.*[24]—Figure 2 shows a plot of $\Delta\nu_{OH}$ *versus* $\Delta\delta_{OH}$. Interestingly, the plot gives a linear relationship independent of types [I] and [II]. The two experimental quantities were related by equation (2). Schaefer [23] has

$$\Delta\delta_{OH} = 0.012\,6\Delta\nu_{OH} + 0.186\ (r\ 0.973) \qquad (2)$$

proposed a linear relationship of the intramolecular hydrogen bond energies E with $\Delta\delta_{OH}$ of the *ortho*-substituted phenols [equation (3), where E is the enthalpy ($-\Delta H$) of intramolecular hydrogen bonding]. The

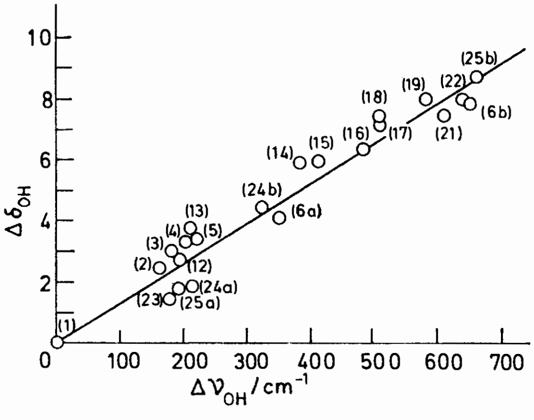


FIGURE 2 Plot of $\Delta\delta_{OH}$ against $\Delta\nu_{OH}$ for intramolecular hydrogen bonds in *ortho*-substituted phenols (for key see Table 2)

$$\Delta\delta_{OH} = -0.4 + E \qquad (3)$$

value of $\Delta\delta_{OH}$ for use in equation (3) is that obtained for CCl_4 solution, $\Delta\delta_{OH}^{CCl_4}$. In n.m.r. spectroscopy, however,

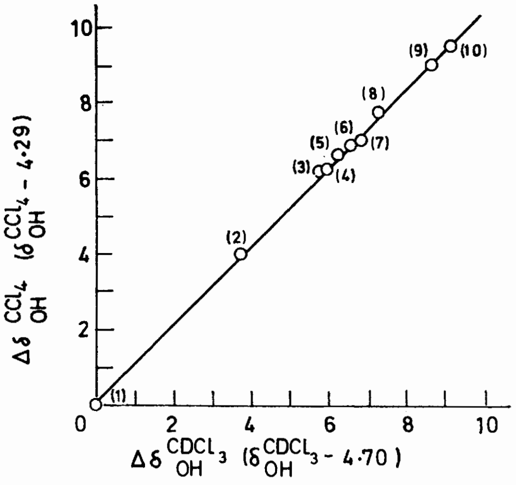


FIGURE 3 Plot of $\Delta\delta_{OH}^{CCl_4}$ against $\Delta\delta_{OH}^{CDCl_3}$ for various intramolecular hydrogen bonding systems: 1, phenol (0, 0); 2, 1-hydroxyfluoren-9-one (4.05, 3.72); 3, 2-nitrophenol (6.22, 5.81); 4, methyl salicylate (6.27, 6.00); 5, salicylaldehyde (6.66, 6.28); 6, 3,5-dichlorosalicylaldehyde (6.94, 6.633); 7, 3-hydroxy-2-acetonaphthone (7.00, 6.82); 8, 2-hydroxyacetophenone (7.78, 7.35); 9, 2-hydroxy-1-acetonaphthone (9.05, 8.72); 10, 1-hydroxy-2-acetonaphthone (9.64, 9.28)

$CDCl_3$ is widely used because of its good solubility for a variety of compounds. Therefore a solvent effect must be considered in estimating E from equation (3) by using the $\Delta\delta_{OH}^{CDCl_3}$ value. We compared $\Delta\delta_{OH}^{CCl_4}$ and $\Delta\delta_{OH}^{CDCl_3}$ observed for phenol derivatives soluble in both CCl_4 and $CDCl_3$, and obtained a good linear relationship as shown in Figure 3, from which equation (4) was derived. From

$$\Delta\delta_{OH}^{CCl_4} = 1.033\,6\Delta\delta_{OH}^{CDCl_3} + 0.096\,1\ (r\ 0.999_4) \qquad (4)$$

equations (3) and (4), we can estimate E values of various compounds soluble in not only CCl_4 but also $CDCl_3$. The E values estimated for the compounds given in Table 2 (E_{est}) were plotted against the $\Delta\nu_{OH}$ values (see Figure 4). The plot gave the linear equation (5).

$$E_{est} = 0.013\,3\Delta\nu_{OH} + 0.59\ (r\ 0.973) \qquad (5)$$

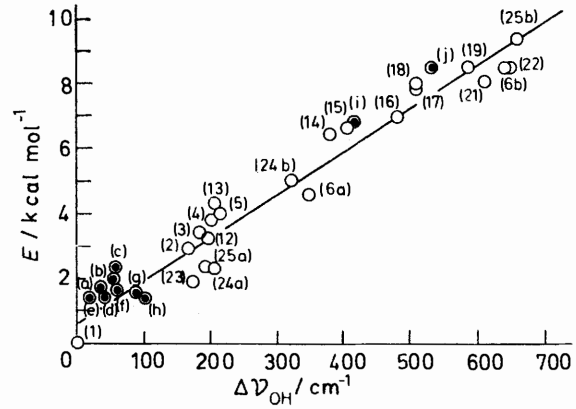


FIGURE 4 Plot of intramolecular hydrogen bond energies E against $\Delta\nu_{OH}$ for *ortho*-substituted phenols [for key see Table 2; also (a), 2-cyanophenol; (b), 2-methoxyphenol; (c), 2-ethoxyphenol; (d), 2-hydroxybiphenyl; (e) 2-fluorophenol; (f) 2-bromophenol; (g), 2-chlorophenol; (i) methyl γ-resocylate; (j), 2,6-diformyl-4-chlorophenol]

The observed E values obtained by other methods were also plotted in Figure 4. Although equation (5) has a tendency to give E values somewhat smaller than the corresponding observed ones, this empirical equation is useful because the approximate value of the intramolecular hydrogen bond energy of *ortho*-substituted phenols can be predicted from the $\Delta\nu_{OH}$ value. In fact, intramolecular hydrogen bond energies for the *ortho*-substituted phenols cannot be readily determined because of the overwhelming predominance of a stable conformer. On the other hand, observation of ν_{OH} in very dilute solution is much easier than that of δ_{OH} or other physicochemical parameters. However, equation (5) is not applicable to a weak hydrogen bond system and one where a strong repulsion between the proton donor and acceptor exists, such as *o*-halogenophenols.[26] Drago and Epley [4] have reported a similar equation for the intermolecular hydrogen bond of substituted phenols with theoretical support for the linear relationship (6). The

$$-\Delta H = 0.010\,3\Delta\nu_{OH} + 3.08 \qquad (6)$$

difference in the constant term between equations (5) and (6) may reflect different interactions in the intra- and inter-molecular hydrogen bonding.

TABLE 3

I.r. spectral data of 2-hydroxybenzyl alcohol

Solvent	Cell length (mm)	Concentration (M)	ν_{OH}/ cm^{-1}	ε/ $mol^{-1}\,l\,cm^{-1}$	$\Delta\nu_{1/2}$/ cm^{-1}	$10^{-4}A_{OH}$/ $mol^{-1}\,l\,cm^{-2}$
$CDCl_3$	3.0	5.980×10^{-3}	3 597	111.6	42.2	1.70
			3 411	71.9	149.6	3.89
$CDCl_3$	0.25	7.848×10^{-2}	3 596	121.1	43.9	1.92
			3 411	81.8	160.1	4.74
C_6D_6	0.25	1.0×10^{-1}	3 555	126.0	64.9	2.96
			3 395	98.4	138.0	4.91

(c) *Geometry of* 2-*Hydroxybenzyl Alcohol*.—From the i.r. spectral data of compounds (1)—(5) (in CCl_4) listed in Table 1, the bands at 3 607 and 3 440 cm^{-1} of 2-hydroxybenzyl alcohol (2) were assigned to a free ν_{OH} band of the CH_2OH group which is a proton acceptor site and to a hydrogen-bonded ν_{OH} band of the phenolic OH group which is a proton donor site. In compounds (4) and (5) only the intramolecular hydrogen-bonded ν_{OH} band was observed; this was taken to indicate that the phenolic OH group is in the completely hydrogen-bonded state. By analogy with the above, the bands at 3 597 and 3 411 cm^{-1} observed for compound (2) in $CDCl_3$ described in Table 3 can easily be assigned. The characteristics of the bands were almost independent of concentration below 0.078M in $CDCl_3$. In C_6D_6, the former band is shifted to lower frequency by the intermolecular hydrogen bonding with the solvent. The n.m.r. spectra of compound (2) in $CDCl_3$ at 39.5 and −17.0 °C are presented in Figure 5. Table 4 gives the corresponding ^{1}H chemical shifts and their assignments. The signals of the CH_2OH group at −17.0 °C show a typical AX_2 spin system, the triplet for the hydroxy proton, the doublet for the equivalent methylene protons, and the coupling constant $^3J_{H,H}$ 6.0 Hz, is observed. The observed equivalence of the methylene protons suggests that compound (2) takes conformation [I] in which the OH group is fixed in the plane of the benzene ring, or indicates a possibly rapid equilibrium between conformers [IIa and b], even at low temperature. The $^3J_{HCOH}$ value of compound (2) is larger than $^3J_{HCCH}$ which is estimated to be *ca*. 3 Hz for a dihedral angle H–C–C–H of 60°.[38] However, the $^3J_{HCOH}$ [39] of 2,2-dimethylpropan-1-ol [40] which does stay predominantly in conformation (IIIa) is 5.7 in CCl_4 and 5.4 Hz in DMSO. At present we do not have evidence allowing unambiguous differentiation between conformations [I] and [II]. Thus, the CNDO/2 calculation for compound (2) was carried out by assuming conformations [I] and [II] and the values were compared with these obtained experimentally.

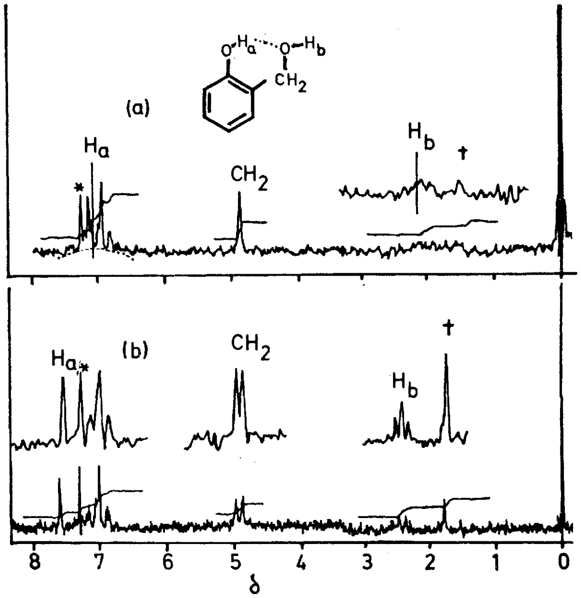


FIGURE 5 N.m.r. spectra of 2-hydroxybenzyl alcohol in $CDCl_3$: (a), 39.5 °C, 0.05M; (b) −17.0 °C, 0.067M. * $CHCl_3$, † impurity in solvent

(d) *Force Constant of the Phenolic* OH *Bond*.—The ν_{OH} band is known to correspond virtually only to an OH stretching mode. For example, the potential energy distribution (p.e.d.) of the ν_{OH} band at 2 850 cm^{-1} of 3-methylthiopentane-2,4-dione, which has very strong intramolecular hydrogen bonding, has even been evaluated as 100% by normal co-ordinate analysis.[41] Indeed, the normal mode for the phenolic OH can be assumed to be approximately equal to a pure OH stretching mode. Assuming a harmonic oscillator model, the force constant k of the phenolic ν_{OH} band was calculated from the second derivative of change in total energy E with OH bond length (R_{OH}) variation near the optimum OH bond length R_{OH°, since the assumption gives the equation[42] $E = 1/2kq^2$ where $k = \partial^2E/\partial q^2$ and $q = R_{OH} - R_{OH^\circ}$. The ν_{OH} value was calculated from the k value by the usual method. The R_{OH°, k, and $\Delta\nu_{OH}$ values obtained from the CNDO/2 calculation are given in Table 5, together with corresponding experimental $\Delta\nu_{OH}$ values. In general, CNDO/2 calculations overestimate the R_{OH° and k values.[34,43] The absolute values calculated for k are very large, but the decrease with increasing hydrogen bond strengths of intramolecular hydrogen bonded conformations for compounds (B)—(D) is consistent with an increase in experimental $\Delta\nu_{OH}$ values. In addition, the calculated $\Delta\nu_{OH}$ values agree reasonably well with the corresponding experimental data in both magnitude and the ordering [(A) < (B_1) < (C_1) < (D) or (A) < (B_2) < (C_2) < (D)]. However, the $\Delta\nu_{OH}$ values of (B_1) and (C_1) are better than those of (B_2) and (C_2) as is evident from Table 5. The calculated R_{OH° values also increase with an increase in the strength of the hydrogen bond. On the other hand, the calculated R_{OH° and k values of phenol (A) and those of non-hydrogen bonded conformations for compounds (B)—(D) are essentially the same.

TABLE 4

N.m.r. spectral data of 2-hydroxybenzyl alcohol

Solvent	Temperature (°C)	Concentration (M)	δ_{OH} [a]	δ_{CH_2}	δ_{OH} [b]
$CDCl_3$	39.5	0.201	~7.1 [d]	4.83	~2.4 [d]
$CDCl_3$	39.5	0.050	~7.1 [d]	4.86	~2.1 [d]
$CDCl_3$–D_2O	39.5	~0.2	*c*	4.80	*c*
$CDCl_3$	−17.0	0.067	7.62 [e]	4.92 (d, ^3J 6.0 Hz)	2.48 (t, ^3J 6.0 Hz)
C_6D_6	39.5	0.1	~7.0 [d]	4.28	

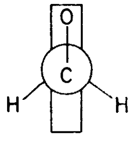
[a] Phenolic OH (intramolecular hydrogen bonding to CH_2OH group). [b] CH_2OH group. [c] Disappeared. [d] Broad. [e] Sharp.

TABLE 5

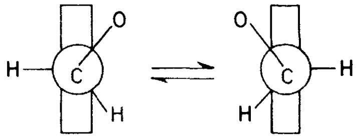
Optimum OH bond lengths, force constants, frequency shifts, and dipole moment derivatives for phenol and *ortho*-substituted phenols by CNDO/2 calculations (experimental values in parentheses)

Compound	ψ_1 (°)	ψ_2 (°)	ψ_3 (°)	ψ_4 (°)	R_{OH° [a]/ Å	K [a]/ mdyn Å^{-1}	$\Delta\nu_{OH}$/ cm^{-1}	$10^{10}\,\dfrac{\partial\mu}{\partial R_{OH}}$ e.s.u.
(A)	0				1.0317	16.699	0 (0)	0.8215 (1.6064)
(B_1)	180	0	0		1.0320	16.698		0.8497
	0	0	0		1.0371	15.541	193 (172)	3.3504 (2.5945)
(B_2)	180	26	7		1.0318	16.692	262	0.9640
	10	26	7		1.0441	15.128	(172)	1.6629 (2.5945)
(C_1)	180	0	0	0	1.0320	16.702	200	0.9325
	0	0	0	0	1.0370	15.506	(206) [b]	3.5937 (2.9046) [b]
(C_2)	180	26	7	−7	1.0318	16.685	271	0.8515
	10	26	7	−7	1.0441	15.073	(206)	2.1666 (2.9046) [b]
(D)	180				1.0324	16.709	477	0.6735
	0				1.0490	13.915	(482)	0.9712 (2.2369)

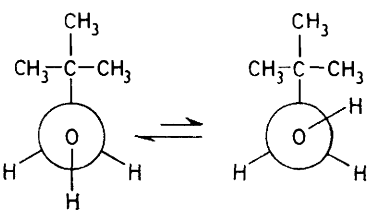
[a] Calculated using least squares quadratic fit using five points taken at 0.01 Å intervals of R_{OH} around the energy minimum. [b] Data for the analogous compound (4) in Table 2 were used for compound (C).



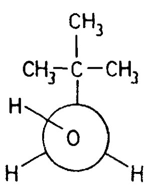
(I)



(IIa) (IIb)



(IIIa) (IIIb)



(IIIc)

(e) *Integrated Intensity of Phenolic* OH.—For a polyatomic molecule, the integrated intensity A_i of the ith band is related to the square of the dipole derivative $\partial\mu/\partial Q_i$ taken with respect to the ith normal co-ordinate (Q_i) by the equation[42,44] $A_i = (N\pi/3c^2)(\partial\mu/\partial Q_i)^2$, where N is Avogadro's number, μ is the molecular dipole moment, and c is the velocity of light. When the normal mode for the phenolic ν_{OH} band is assumed to be a pure stretching mode as mentioned above, the dipole moment derivative on the stretching mode can be calculated approximately by the equation[42] $\partial\mu/\partial R_{OH} = (1/m_H + 1/m_O)^{-\frac{1}{2}}\partial\mu/\partial Q$, where μ is the molecular dipole moment in the direction of the phenolic OH axis, and m_H and m_O are the masses of the hydrogen and oxygen atoms, respectively. Figure **6** indicates variations in the dipole moment of phenol (A) and intramolecular hydrogen bonded conformations for compounds (B)—(D) as a function of the OH bond length. The calculated $\partial\mu/\partial R_{OH}$ values at the optimum OH bond length obtained by the least squares method are given in Table 5, together with the corresponding experimental values. The calculated values for phenol (A) and intramolecular hydrogen bonded conformations for compounds (B)—(D) run closely parallel with the experimental ones. The experimental values of compounds (B) and (C) are intermediate between the calculated $\partial\mu/\partial R_{OH}$ values for the planar and non-planar conformations of each compound. In spite of the fact that salicylaldehyde (D) shows the strongest hydrogen bonding in Table 5, its $\partial\mu/\partial R_{OH}$ value is smaller than those for compounds (B) and (C). This suggests theoretically that much delocalization of the OH bond electron occurs in compound (D), which also applies to other conjugated, chelated compounds.

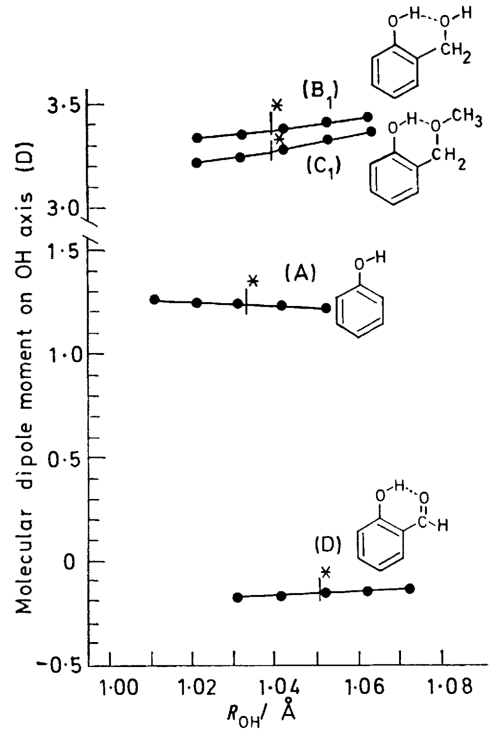


FIGURE 6 Variations of the calculated dipole moments as a function of the OH bond length (R_{OH}). * Optimum OH bond length ($R_{OH}°$)

(f) *Intramolecular Hydrogen Bond Energy*.—The calculated energy difference ΔE between the *cis*- and *trans*-conformers and the corresponding experimental data for compounds (B)—(D) are presented in Table 6. The results show that the calculated values agree reasonably with the experimental data, although the calculated ΔE value of compound (C) is slightly smaller than that of compound (B) in contrast to the observed $\Delta\nu_{OH}$ value. The calculated values (B$_2$) and (C$_2$) are larger than those of (B$_1$) and (C$_1$), respectively. The experimental value of (B) or (C) is intermediate between the calculated values of (B$_1$) and (B$_2$) or those of (C$_1$) and (C$_2$).

In conclusion, two kinds of correlation for the systems studied were found between $\Delta\nu_{OH}$ and A_{OH}, and a linear relationship between $\Delta\nu_{OH}$ and $\Delta\delta_{OH}$, independent of the above two types, was also found. The observed values of $\Delta\nu_{OH}$ can be used as a measure of intramolecular hydrogen bond strength in analogous compounds. The mutual correlation described here should be useful for predicting molecular configurations. The CNDO/2 method predicts fairly reasonable values of OH stretching frequency shifts and integrated intensities, OH bond lengths, and hydrogen bond energies in the systems examined.

TABLE 6

Intramolecular hydrogen bond energies for *ortho*-substituted phenols calculated by the CNDO/2 method and from experimental data (kcal mol^{-1})

Compound	CNDO/2 ΔE(*cis*→*trans*) [a]	Experimental
(B$_1$)	1.50	2.98,[d] 2.88 [e]
(B$_2$)	4.98	
(C$_1$)	1.20	3.86,[d] 3.06 [e]
(C$_2$)	4.75	
(D)	6.27 (7.44) [b]	7.09,[c] 6.99,[d] 7.00 [e]

[a] R_{OH} = 0.96 Å. [b] Ref. 26; *ab initio* calculation. [c] Estimated from equation (3).[23] [d] Estimated from both equations (3) and (4).[23] [e] Estimated from equation (5).

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