939. *The Association of* ortho-*Substituted Phenols with Ethers.*

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The association of substituted phenols with various types of ether has been studied spectroscopically. Systematic variations were made in the numbers and sizes of the alkyl substituents of the phenols and of the ethers. The results show that with minor exceptions (particularly 2,6-di-t-butylphenol) changes in the sizes of the substituents do not materially affect the strength of the hydrogen bond formed, as measured by $\Delta\nu$(OH), but do lead to quite large alterations in the equilibrium coefficients. This is attributed to entropy changes and it is suggested that the present method provides a way in which the two components of the free energy of the hydrogen bond (bond strength and entropy) may be differentiated and compared.

THERE have been several spectroscopic studies on " hindered phenols," which are generally regarded as all those with 2,6-dialkyl substituents. Most of these have been concerned with the liquid or the solid phase in which the stretching frequencies of the associated hydroxyl groups occur at higher values than in normal phenols.[1-3] This is ascribed to steric effects which limit the association to weakly bonded dimers instead of the usual polymers. Puttnam [2] suggested that steric effects may also occur in *o*-t-butylphenol as this compound shows two free ν(OH) bands in solution which could be derived from *cis*- and *trans*-arrangements of the H–O–Ph group with respect to the *o*-alkyl substituent.

In contrast, Bellamy and Williams [3] have shown that the relative strength of the hydrogen bonds formed between solvents and mono- or di-*o*-alkylphenols (other than 2-6-di-t-butylphenol) are not affected by the physical size of the alkyl group. The free energy of association may be regarded as composed of two components, a bond strength and an entropy term, and these are not necessarily interrelated. Studies of the equilibrium coefficient K provide a measure of the whole, whilst frequency shifts provide a measure only of the first term as they are determined by the changes in the O–H bond stretching force constant.

From studies on both K and $\Delta\nu$ it should, therefore, be possible to differentiate between two different kinds of steric effect. There are those—here termed " physical " effects—which lead to a reduction in the force constant of the hydrogen bond due to an otherwise unnatural O • • • O distance, and those which arise simply from variation in the entropy term. It is, for example, possible to envisage a series of different compounds, all forming hydrogen bonds of the same strength with a given acceptor, but showing variations in their equilibrium coefficients because steric effects influence the ability of the hydrogen bond, once broken, to be re-formed with consequent change in the entropy term.

We have therefore studied the association of a range of *ortho*-substituted phenols with ethers which themselves comprise alkyl groups of various sizes. Bistrimethylsilyl oxide with an Si–O–Si angle [4] of 130° has been included as being somewhat similar in shape to di-t-butyl ether and as being likely to produce considerable steric effects. It was hoped in this way to decide the sizes of the groups necessary for a measurable change in the O • • • O distance. At the same time we measured the equilibrium coefficients for the association of the phenols with ethers, in a standard solvent under fixed conditions, in order to measure the total free-energy change.

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[1] Sears and Kitchen, *J. Amer. Chem. Soc.*, 1949, **71**, 4110; Coggeshall, *ibid.*, 1947, **69**, 1620; 1950, **72**, 2836; Coggeshall and Saier, *ibid.*, 1951, **73**, 5414; Friedel, *ibid.*, 1951, **73**, 2881.

[2] Puttnam, *J.*, 1960, 486, 5100.

[3] Bellamy and Williams, *Proc. Roy. Soc.*, 1960, *A*, **254**, 119.

[4] Yamasaki, Kotera, Yokoi, and Ueda, *J. Chem. Phys.*, 1950, **18**, 1414; Roth, *Ann. Rev. Phys. Chem.*, 1951, **2**, 217.

EXPERIMENTAL

The materials were of commercial origin, except di-t-butyl ether,[5] 2,6-diethylphenol,[3] *o*-t-butylphenol, and bistrimethylsilyl oxide, the last two kindly supplied respectively by Mr. Ivor Brown and Dr. Vincent Davies of Imperial Chemical Industries Limited. The compounds were purified, dried, and checked by gas–liquid chromatography before use.

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 in. (2000—3656 cm.$^{-1}$)] operated under both dry-air and vacuum conditions. The wave-number scale calibration was checked against the spectra of water vapour and ammonia before and after each interrupted group of measurements. Frequency measurements for the " free " and ether-associated hydroxyl bands are believed to be accurate to ±1 and ±2 cm.$^{-1}$, respectively.

TABLE 1.

Hydroxyl stretching frequencies (cm.$^{-2}$) of alkyl-substituted phenols.

(Apparent extinction coefficients, ε_a, in parentheses.)

State/Subst.	None	2-Me	2-Pr^i	2-Bu^t	2-Bu^t, 5-Me
Vapour †	3654	*	3654	*	*
Liquid	—	—	—	~3600sh	3606
	~3510sh	~3550sh	3533sh	3535	3528
	~3350br	~3395br	3460br	Tail	Tail
Hexane	3622	3623	3625	3655 3616	3655 3616
CCl$_4$	3612(205)	3613(165)	3615	3647(25) 3606(200)	3647(15) 3608(170)
Tetrahydrofuran	3287vbr †	3304(175)	3303 †	3299(180)	3307(180)
Diethyl ether	3344 †	3341(165)	3338 †	3337(170)	3343(170)
Di-isopropyl ether	3625vw	3627vw	3620vw	—	
	3329(180)	3332(160)	3330(160)	3324(175)	3335(160)
Di-n-butyl ether	3620vw	3620vw	3622(5)	3613vw	3615(5)
	3336(170)	3345(140)	3341(145)	3338(165)	3342(155)
				3650vw	
Di-t-butyl	3618vw	3623(10)	3613vw	3613vw	3613vw
	3306(130)	3318(115)	3310(120)	3305(120)	3314(55)
				3655(15)	*
Bistrimethylsilyl oxide	3621(80)	3623(80)	3621(75)	3615(70)	3616(75)
	3448(80)	3456(45)	3449(55)	3442(65)	3451(55)

State/Subst.	2,6-Me$_2$	2,6-Et$_2$	2,6-Pr$^i_2$	2,6-Bu$^t_2$	4-Me, 2,6-Bu$^t_2$
Vapour †	3654	3652	3650	*	3671
Liquid	—	3622sh †	3618	3644	3648 †
	3573	3583 †	3577	—	—
	3500sh	*	Tail	—	—
Hexane	3629	3629	3627	3653	3655
			3642sh		
CCl$_4$	3621(155)	3623	3620(145)	3647(240)	3651
Tetrahydrofuran	3503vwsh †			3641(45)	3645,† 3536 †
	3383br †	3405br †	3410 †	3545(70)	3400 †
Diethyl ether		3620 †	3624 †	3649(115)	3651 †
	3407 †	3412 †	3428 †	3385(25)	
Di-isopropyl ether	3629(15)	3629(20)	3629(20)	3650(155)	3654(145)
	3398(90)	3400(90)	3410(85)	3404vw	3450(10)
Di-n-butyl ether	3628(15)	3627(25)	3625(30)	3650(150)	3651(145)
	3407(85)	3421(75)	3435(65)	3383vw	3405(10)
Di-t-butyl ether	3629(40)	3628(45)	3627	3651(200)	3654(195)
	3418(60)	3424(60)	3425	—	3475(5)
Bistrimethylsilyl oxide	3627(110)	3628(130)	3627(125)	3653(160)	3654(215)
	3545(15)	—	—	—	—

* Not measured. — No absorption. Tail = absorption diminishing slowly towards lower frequencies. † Values taken from ref. 3.

The linearity of the percentage transmission scale was checked by Shrewsbury's procedure,[6] and

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[5] Erickson and Ashton, *J. Amer. Chem. Soc.*, 1941, **63**, 1769.

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

intensities were measured on bands of $\nless 10\%$ transmission. The theoretical spectral slit-width, computed from tables supplied by Unicam Instruments Ltd., was approximately 5·5 cm.$^{-1}$ at 3600 cm.$^{-1}$, and 4·5 cm.$^{-1}$ at 3350 cm.$^{-1}$. The region 300—3660 cm.$^{-1}$ was scanned at 33 cm.$^{-1}$ per min. and the " free " hydroxyl bands near 3600 cm.$^{-1}$ were scanned for a second time at 16 cm.$^{-1}$ per min. 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 absorption of the solution (determined with solvent in the reference beam). The integrated absorption intensities, A and $A°$ (Table 2), of the free hydroxyl bands were calculated by the method of direct integration due to Ramsay [7] and are in l. mole^{-1} cm.$^{-2}$. Approximate integrated absorption intensities, A, of the more asymmetrical, associated hydroxyl peaks were obtained by averaging areas calculated by use of $\Delta\nu_{\frac{3}{4}}^{a}$, $\Delta\nu_{\frac{1}{2}}^{a}$, and $\Delta\nu_{\frac{1}{4}}^{a}$, according to the improved, direct, integrated-intensity measurement technique of Cabana and Sandorfy.[8]

TABLE 2.

Integrated absorption intensity data (A) for hydroxyl stretching bands of *o*-alkylphenols in 0·5M-ether–carbon tetrachloride solution.

Subst.:		None		2-Me		2-Pr^i		2-Bu^t	
Dissolved ether		ν(OH)	$10^{-4}A$	ν(OH)	$10^{-4}A$	ν(OH)	$10^{-4}A$	ν(OH)	$10^{-4}A$
Tetrahydrofuran	free	3611	0·225	3613	0·310	3612	0·280	3647 3606	0·075 0·275
	assoc.	3321	9·00	3329	8·85	3329	8·70	3332	8·60
Diethyl ether	free	3611	0·345	3613	0·410	3613	0·400	3648 3607	0·095 0·360
	assoc.	3334	7·30	3340	6·65	3340	6·25	3338	6·20
Di-isopropyl ether	free	3611	0·300	3613	0·430	3612	0·400	3647 3607	0·080 0·335
	assoc.	3314	8·00	3322	7·00	3325	7·00	3325	7·10
Di-n-butyl ether	free	3612	0·390	3614	0·510	3613	0·430	3648 3607	0·100 0·410
	assoc.	3330	6·65	3335	5·80	3336	5·35	3336	5·95
Di-t-butyl ether	free	3610	0·450	3613	0·590	3612	0·575	3648 3607	0·105 0·505
	assoc.	3297	7·35	3314	5·90	3325	5·85	3336	5·05
Bistrimethylsilyl oxide	free	3611	1·00	3613	1·10	3612	1·10	3648 3607	0·170 0·945
	assoc.	3454	1·85	3464	1·45	3462	0·650	3447	0·780

Subst.:		2,6-Me$_2$		2,6-Pr$^i_2$		2,6-Bu$^t_2$	
Dissolved ether		ν(OH)	$10^{-4}A$	ν(OH)	$10^{-4}A$	ν(OH)	$10^{-4}A$
Tetrahydrofuran	free	3619	0·490	3618	0·520	3647	1·45
	assoc.	3400	4·30	3426	3·45	3557	0·530
Diethyl ether	free	3620	0·710	3619	0·740	3647	1·35
	assoc.	3409	2·35	3436	2·05	—	
Di-isopropyl ether	free	3620	0·725	3619	0·765	3647	1·25
	assoc.	3395	2·15	3412	1·65	—	
Di-n-butyl ether	free	3620	0·720	3619	0·830	3647	1·30
	assoc.	3401	1·80	3426	1·75	—	
Di-t-butyl ether	free	3621	0·845	3619	0·845	3648	1·30
	assoc.	3424	1·35	3430	0·985	—	
Bistrimethylsilyl oxide	free	3621	0·925	3619	0·895	3648	1·20
	assoc.	—		—		—	

Apparent half-band widths were as follows: free OH bands, 18 ± 2 cm.$^{-1}$, except the band near 3650 cm.$^{-1}$ in *o*-t-butylphenol (~24 ± 1 cm.$^{-1}$); associated OH bands varied from 150 to 270 cm.$^{-1}$ with no apparent regularity.

The integrated absorption intensities of the phenols in CCl_4, $10^{-4}A°$, were phenol 1·20, 2-Me 1·05, 2-Pr^i 1·10, 2-Bu^t 0·95, 2,6-Me$_2$ 0·95, 2,6-Pr$^i_2$ 0·90, and 2,6-Bu$^t_2$-phenol 1·30.

For the determination of K values (Table 3) for the association of the phenols with the ethers in the mixed solvents, the solutions in carbon tetrachloride were 0·1 ± 0·002M with respect to the phenols and 0·5 ± 0·002M with respect to the ethers. In such solutions there is very little self-association and it is reasonable and convenient to assume that only phenol–ether interactions are involved. Measurements were made immediately after the solutions

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[7] Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

[8] Cabana and Sandorfy, *Spectrochim. Acta*, 1960, **16**, 335.

had been prepared, the same pair of cells being used throughout. The solutions were allowed to reach the temperature (29° ± 2°) of the sample well of the instrument before the spectra were recorded. Solvent–solvent backgrounds were run immediately before every determination.

$A°$ values were determined for CCl_4 solutions in 5 mm. cells, and at 0·003M-concentration to ensure that all the phenol present was in the monomer form. The proportion of free phenol in the mixed solvents was determined by parallel measurements on the unassociated hydroxyl band. This involves the assumption that the presence of the small amount of ether will not change the absolute integrated intensity, A, of the unassociated band. This is reasonable in view of the small concentration of the ethers and of the fact that the unassociated hydroxyl frequencies are the same as they are in pure CCl_4 solution (Tables 1 and 2). Graphical separation of the bands was unnecessary (cf. Figure).

The K values (l. mole^{-1}) were determined from $A°$ and A as follows:

For acid (a) and base (b) association,

$$\mathrm{a} + \mathrm{b} \rightleftharpoons \mathrm{a} \cdots \mathrm{b},$$

the equilibrium constant $k = [\mathrm{a} \cdots \mathrm{b}]/[\mathrm{a}][\mathrm{b}]$.

Then, if c_a = total concentration of acid (mole l.$^{-1}$), c_b = total concentration of base (mole l.$^{-1}$), $A°$ = integrated intensity of ν(OH) in CCl_4 (all " free," *i.e.*, equivalent to A values at zero ether concentration), and A = integrated intensity of ν(OH) free (unassociated) in the mixed ether–CCl_4 solvent, then

$$k = \frac{1 - A/A°}{A/A°[c_b - c_a(1 - A/A°)]}$$

Results.—The results are summarised in Tables 1—3 and illustrated in the Figure. Table 1 gives the values of ν(OH) of the various phenols in various states and in the ethers; Table 2 covers dilute solutions of phenols in binary mixtures of ethers and carbon tetrachloride. Table 3 lists the Δν values and the equilibrium coefficients for many of these systems, under conditions of arbitarily fixed concentrations and temperature.

TABLE 3.

Equilibrium constants (K) * for phenol–ether association at 29° ± 2°.

Hydroxyl frequency shifts, $\Delta\nu = \nu^{\mathrm{hexane}}_{(\mathrm{OH})} - \nu^{\mathrm{ether/CCl_4}}_{\mathrm{OH}}$, are in parentheses.

	Ether					
Subst.	THF †	Et_2O	Pr^i_2O	Bu^n_2O	Bu^t_2O	$(Me_3Si)_2O$
None	10·4(301)	6·0(288)	7·2(308)	4·9(292)	3·9(325)	0·4(168)
2-Me	5·5(294)	3·4(283)	3·2(301)	2·6(288)	1·7(309)	0(159)
2-Pr^i	6·7(296)	3·9(285)	3·9(300)	3·0(289)	2·0(300)	0·06(163)
2-Bu^t ‡	5·7(284)	3·7(278)	4·1(291)	2·9(280)	2·3(280)	0(169)
2,6-Me$_2$	2·0(229)	0·67(220)	0·62(234)	0·63(228)	0·22(205)	0·03(—)
2,6-Pr$^i_2$	1·7(201)	0·51(191)	0·48(215)	0·23(201)	0·19(197)	0·06(—)

* l. mole^{-1}. † Tetrahydrofuran. ‡ Calculations involve band at 3610 only.

K values for 2,6-Bu$^t_2$ phenol are all approx. zero.

The extremely weak associated hydroxyl absorptions for 2,6-dimethylphenol and 2,6-di-iso-propylphenol in 0·5M-$(Me_3Si)_2O$–CCl_4 could not be accurately located and are not quoted. For the same reason, Δν values are not available for 2,6-di-t-butylphenol in any of the 0·5M-ether–CCl_4 solvents.

DISCUSSION

The proton-donor and -acceptor properties in an acid–base system will determine a characteristic O–H ··· O distance for the hydrogen bond. This may then be modified by any steric effects operating from either side. The Δν values of ν(OH) are directly related to the final O ··· O distances,[9] and therefore provide a guide to the resultant of these effects. With unhindered phenols, it is known that the hydroxyl frequencies vary systematically with the basicity of the solvent in such a way that the Δν/ν values of any one donor in a series of solvents can be plotted directly against the corresponding values of any other in the same solvents, to give a straight line.[3] In any instance in which steric

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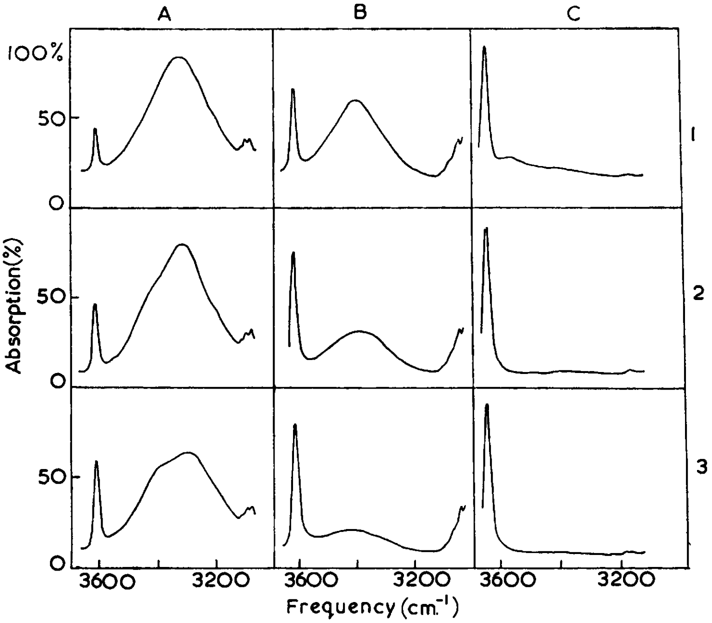
[9] Nakamoto, Margoshes, and Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480.

effects lead to a larger O • • • O distance than would be expected from the acid–base properties, a deviation from this straight line will occur, and in principle it should be possible to derive the change in O • • • O distance which has resulted. It has already been shown in this way that 2,6-di-t-butylphenol is subject to considerable steric hindrance to solvent association, but that other 2,6-dialkylphenols give normal plots.[3] Application of this technique to our new results should give a clear indication of the presence or absence of this kind of " physical " steric effect with the variously hindered ethers. The Δν/ν values themselves are also informative in providing a direct measure of the hydrogen bond strength. For any one phenol they should, therefore, change systematically with the basicity of the ether, unless " physical " steric effects intervene. However, the equilibrium coefficients measured in carbon tetrachloride will be determined both by the strengths of the hydrogen bonds, and by the entropy effects and will not necessarily follow the same pattern.



Hydroxyl absorptions of (A) phenol, (B) 2,6-dimethylphenol, and (C) 2,6-di-t-butylphenol (0·1M; in 0·5 mm. cells) in (1) 0·5M-tetrahydrofuran–CCl_4, (2) 0·5M-di-isopropyl ether–CCl_4, and (3) 0·5M-di-t-butyl ether–CCl_4.

Δν/ν *Plots*.—The data for the solvent shifts of ν(OH) for many of the phenols now studied are already available.[3] Inclusion of the new data in Tables 1 and 2 on the original plots (Fig. 1 of ref. 3) shows that in the great majority of cases the points fall on the lines within the limits of experimental error. 2,6-Di-t-butyl phenol, of course, shows marked steric effects with all the ethers studied, and none of the 2,6-dialkylphenols associates to an appreciable extent with bistrimethylsilyl oxide, although the monoalkylphenols associate normally. However, only in the case of di-t-butyl ether does there appear to be any other steric hindrance effect resulting in weaker hydrogen bonds, and even this is small The point for *o*-isopropylphenol in this solvent is very slightly displaced from the standard line, in a direction indicating an increased O • • • O distance, and the effect increases with the degree of substitution of the phenol. However, the effect is not large and even in the more hindered phenols the displacement is only slightly greater than the experimental error. Clearly, the steric effects on the hydrogen-bond strength are too uncommon in this series, and too small, to be capable of interpretation in terms of the alterations they produce in the O • • • O distances.

$\Delta\nu$ *Values.*—For unhindered phenols the $\Delta\nu$ values vary systematically with the basicity of the ethers and follow the same order as phenol itself, *i.e.*, $Bu^t_2O > Pr^i_2O >$ Tetrahydrofuran $> Bu^n_2O > Et_2O \gg (Me_3Si)_2O$. Table 3 shows that this order is effectively maintained for all the phenols up to the 2,6-di-t-butyl derivative, the only exception being with di-t-butyl ether. This ether moves down the list as an effective acceptor as the sizes of the substituents of the phenol are increased, a result in line with the findings given above. Exceptionally, in the silyl ether the changes in $\Delta\nu$ values are all small, indicating that the hydrogen bonds formed are of comparable strengths.

The slopes of the $\Delta\nu/\nu$ curves for 2,6-dialkylphenols show them to be less acidic than either phenol or its monoalkyl derivatives. This is reflected in the $\Delta\nu$ values in ether, which are smaller by some 60—70 cm.$^{-1}$. This change is too great to be attributed wholly to the inductive effects of the alkyl groups, and in the absence of " physical " steric hindrance it must arise from some dipolar interaction between the hydroxyl and the alkyl groups which reduces the acidity of the former.

The $\Delta\nu$ values for the liquid phenols are also of interest (Table 1). Mono-*o*-alkylphenols (with the exception of a t-butylphenol) show values typical of the usual polymeric self-association, but as earlier workers have found, 2,6-dialkylphenols show only small shifts ($\sim$45 cm.$^{-1}$) away from the monomeric value. If it is accepted that 2,6-di-isopropylphenol is able to form strong hydrogen bonds with say di-isopropyl ether, it is difficult to see why the dialkylphenols should not self-associate freely. Indeed, it would seem that they do (with the exception of 2,6-di-t-butylphenol), at least as far as the dimer stage, as the $\Delta\nu$ values are normal for dimeric association when account is taken of their reduced acidity. According to Puttnam [2] the $\Delta\nu$ value for liquid dimeric phenol is 107 cm.$^{-1}$ and that of the 2,6-dialkyl dimers is about 65 cm.$^{-1}$. The ratio is almost exactly that which would be predicted from the $\Delta\nu/\nu$ plots [3] based on associations with solvents with which no " physical " steric hindrance occurs, and in which the differences in $\Delta\nu$ values arise solely from acidity effects. Further the $\Delta\nu$ values and therefore the hydrogen bond strengths, of 2,6-dimethyl-, 2,6-diethyl-, and 2,6-di-isopropyl-phenol are all essentially the same and do not show the regular changes which might be expected from a change in the steric hindrance. The problem appears to be, therefore, not one of whether these materials are able to self-associate, but why, having done so, they are unable to continue the process by the addition of further units. This problem is intimately connected with the reasons for the strengthening of the hydrogen bonds in polymeric as against dimeric alcohols. Weltner and Pitzer [10] and Pauling [11] suggested many years ago that polymeric alcohols and phenols took a cyclic structure and that the bonds were stronger than those of the dimer for this reason. The present findings also appear to support this view. In the association of say, 2,6-di-isopropylphenol, any " physical " steric hindrance present would be limited to the interaction between one of the isopropyl groups of each unit. No greater interaction could arise to prevent the addition of a third unit to form a trimer, unless this unit were seeking to make up a cyclic system. In the last case, steric interactions would be operating on the isopropyl groups on both sides of the third unit and could well prevent further association. We therefore conclude that dimeric association occurs normally in these phenols and that the differences between them and normal phenols arise from their inability to take up cyclic polymeric forms.

Equilibrium Coefficients.—In the present studies the concentrations of the phenol and ether components in carbon tetrachloride have been maintained at arbitary values, as has the temperature. The observed equilibrium coefficients will depend upon (*a*) the strength of the hydrogen bonds which determine how readily the bonds will be broken and (*b*) the entropy effects which are related to the readiness with which a broken bond will be

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[10] Weltner and Pitzer, *J. Amer. Chem. Soc.*, 1951, **73**. 2606.

[11] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 3rd edn., 1960, p. 474.

re-formed. Under the conditions chosen the number of collisions between phenol and ether molecules at any one moment will be more or less the same in all cases. The variations in entropy arise from the fact that the shapes of the donor and the acceptor molecule play a large part in determining what proportion of the collisions leads to hydrogen-bond formation. Large differences due to this effect have already been demonstrated qualitatively in this series.[3]

The experimental values of K for the chosen conditions are given in Table 3; they follow a consistent pattern. For any one phenol the K values do not follow in any way the basicity of the ethers, as do the $\Delta\nu$ values, but instead arrange themselves in the order of the steric complexity of the ethers. The order of effectiveness in maintaining the hydrogen bond is, therefore, tetrahydrofuran $> Et_2O, Pr^i_2O > Bu^n_2O > Bu^t_2O \gg (Me_3Si)_2O$. However, apart from bistrimethylsilyl oxide, there are only small differences (13—37 cm.$^{-1}$) in the $\Delta\nu$ values for any one phenol with the various ethers, showing that the hydrogen bonds are of closely similar strengths. The contributions of the bond strength term in the free energy of association are therefore nearly constant and the considerable variations in K must arise from alteration in the entropy term, the changes in the shapes of the acceptor molecules playing a decisive part in determining the number of effective collisions which lead to association. Some part of the low K values found for the bistrimethylsilyl oxide is, of course, due to the weaker hydrogen bond, but even here entropy effects may be dominant.

A similar effect is found on passing down the columns of Table 3. The nature of the ether is now constant and the complexity of the phenol increases. In any single ether, the $\Delta\nu$ values show that phenol and its monoalkyl derivatives form hydrogen bonds of very similar strengths. Despite this, the K values change greatly as alkyl groups are introduced. Some part of the lowering of the K values found for the 2,6-dialkylphenols must be attributed to their lower acidity, but the changes are too great to be due to this alone and entropy changes must play a major part.

As expected, the incidence of entropy effects amongst the various phenols becomes more and more apparent as the complexity of the ethers is also increased. Thus the K value of phenol changes by a factor of 2·7 on passing from tetrahydrofuran to di-t-butyl ether, but the corresponding value for 2,6-di-isopropylphenol is a factor of 9. The impact of these effects in terms of the relative heights of the free and the associated peaks is very marked, and a few typical examples are illustrated in the Figure. The differences are unmistakable and could well form the basis of diagnostic techniques for the identification of substitution patterns in phenols and possibly in more complex molecules such as the sterols and triterpenes.

The Monomeric Hydroxyl Frequencies.—The values in Table 1 confirm the findings of Puttnam,[2] von Dohlen,[12] and Goddu [13] that there are two monomeric hydroxyl frequencies in some cases. One of these is at the normal value for alkylphenols, and the other is about 40 cm.$^{-1}$ higher. 5-Methyl-2-t-butylphenol, for example, shows bands at 3608s and 3647w cm.$^{-1}$, and *o*-t-butylphenol behaves similarly. Only the higher frequency absorption is shown by 2,6-di-t-butylphenol. This must indicate some steric interaction between the t-butyl and the hydroxyl group when the latter is turned towards the former. For example, the hydroxyl group might be twisted out of the plane of the ring in the *cis*-configuration, as previously suggested and since discounted by Puttnam.[2] However, in view of the high intensity of the hydroxyl band of 2,6-di-t-butylphenol, it is perhaps more likely that there is a small opening out of the C–O–H angle whereby the coplanarity of these bonds with the ring is retained.

Conclusions.—These results confirm the view that " physical " steric hindrance plays a part in preventing or weakening the association of 2,6-di-t-butylphenol with many solvents, and show that similar effects probably occur with other 2,6-dialkylphenols dissolved in

[12] Von Dohlen, personal communication.

[13] Goddu, *J. Amer. Chem. Soc.*, 1960, **82**, 4533.

bistrimethylsilyl oxide. There is also a slight weakening of the hydrogen bonds formed when some alkylphenols associate with di-t-butyl ether. These effects also appear to play a part in preventing cyclic polymeric association in *o*-t-butylphenol and in all the 2,6-dialkylphenols, although dimerisation occurs normally.

In all the other systems studied, variations in the sizes of alkyl groups on the donor or acceptor do not prevent the formation of hydrogen bonds of normal strength but do produce alterations in the equilibrium coefficients. This is attributed to a change in the proportion of collisions which are fruitful in leading to hydrogen-bond formation (entropy effects) and is not associated with any weakening of the bond once formed. This technique provides a simple method whereby entropy effects of this type can be compared, and it would seem that they are surprisingly large. Similar entropy effects would be expected to play an important part in the reaction kinetics of these materials, and some correlation should exist between the two, particularly in reactions involving a transition state formed through a hydrogen bond. There is also a reasonable parallel between the *K* values given above and the relative amounts of substituted phenols absorbed on charcoal from hexane solution, as reported by Wheeler and Lacey.[14]

The fact that the hydrogen atoms of many of these phenols are able to form normal associations not affected by " physical " steric hindrance does not, of course, imply that they can equally readily be replaced at the same point in space by larger groups. Steric hindrance effects are, therefore, to be expected in many of the reactions of compounds of this series despite the fact that proton donation can usually occur normally.

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[14] Wheeler and Lacey, *Canad. J. Chem.*, 1959, 1235.