fore, the importance of $\phi_e^{(2)}$ with respect to ϕ_g will diminish sharply with decreasing k_λ, and at infrared frequencies the OR depends only on ϕ_g and not on $\phi_e^{(2)}$. It may therefore be concluded that our theory gives an adequate description of the OR of molecules of the type CHDXY for infrared light and that we are not sure whether or not the omission of $\phi_e^{(2)}$ is permissible for visible or ultraviolet light.

Steric Effects on Hydrogen Bonding[1]

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Abstract: Quantitative thermodynamic studies of the hydrogen bonding of sterically hindered alcohols and phenols with donors have been carried out. The enthalpies of hydrogen bonding between hindered hydroxy groups and donors are appreciable and are comparable to those with simple alcohols and phenols. The low equilibrium constants are mainly due to entropy factors. $\Delta\nu_{OH}$ and ΔH° are not linearly related in the sterically hindered systems. Electrical effects of *para* substituents on the hydrogen bonding of *para*-substituted 2,6-di-*t*-butylphenols with donors have been studied and the results do not show a linear free energy relationship.

It has been known that sterically hindered phenols ("kryptophenols") do not undergo characteristic reactions of simple phenols.[2] Sterically hindered alcohols and phenols have also been found to be less associated than simple hydroxy compounds[3,4] and the low equilibrium constants of self-association were found to be due to entropy factors, since the enthalpies were quite large in these systems. Recent studies of Bellamy and co-workers[5,6] have shown that the relative strengths of hydrogen bonds between donors and mono- or di-*o*-alkylphenols are not greatly affected by the bulk of the alkyl groups except in the case of di-*o*-*t*-butylphenol. These conclusions of Bellamy and co-workers were based on measurements of frequency shifts, $\Delta\nu_{OH}$, and a few equilibrium constants for the interaction between the hindered phenols with ethers. The hydrogen bonding of several hindered alcohols and phenols with a variety of donors has been reported in the present communication.

Bellamy and co-workers[5,6] assumed the enthalpy of hydrogen bonding to be proportional to the $\Delta\nu_{OH}$; thus, on the basis of the low $\Delta\nu_{OH}$ 2,6-di-*t*-butylphenol was considered to form weak hydrogen bonds with donors. Our recent studies of the self-association of hindered alcohols and phenols[4] and of hydrogen bonding between various donors and acceptors[7] indicated to us that a linear $\Delta\nu_{OH}$–ΔH° relation does not hold when one considers hydrogen bonding of a variety of hydroxylic compounds with donors. It was therefore decided to investigate the thermodynamics of hydrogen bonding of hindered alcohols and phenols with a donor in detail to establish quantitatively the steric effects on the equilibrium constants, the frequency shifts, and the enthalpy of hydrogen bonding. In addition to examining steric effects in hindered phenols, electrical effects of *para* substituents on the hydrogen bonding of sterically hindered phenols have also been studied.

Results and Discussion

Hydrogen bonding data of several mono- and di-*ortho*-substituted phenols with a few donors have been compared with the data on phenol in Table I. It can be clearly seen that in all the cases the equilibrium constants and the $\Delta\nu_{OH}$ decrease with the increase in the bulk of the *ortho* substituents. Steric effects on equilibrium constants and $\Delta\nu_{OH}$ are also quite marked in the hindered alcohols (Table II). These results are similar to those of Bellamy and co-workers,[5,6] but unfortunately the data could not throw any light on the strengths of the hydrogen bonds and the cause for the dimunition of equilibrium constants.

Blue shifts of n–π^* transitions[8] of carbonyl and thiocarbonyl groups in the sterically hindered alcohols were also found to be considerably smaller than in simple alcohols. Since n–π^* blue shifts are proportional to hydrogen bond energies,[7,9] this may be taken as evidence of weak hydrogen bonding between the sterically hindered alcohols and donors. However, in the present case, comparison of blue shifts is not valid since there will be little or no self-association of sterically hindered alcohols[4] when used as solvents while other simple alcohols will be highly associated.[10] Relative comparisons of hydrogen bond energies in terms of blue shifts would be possible only if the magnitude of self-association of alcohols is about the same.

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(1) Forms part of the material for the Ph.D. thesis of S. Singh to be submitted to the Indian Institute of Technology, Kanpur, India. All correspondence should be addressed to C. N. R. R.

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Table I. Hydrogen Bonding of Hindered Phenols ($R_1R_2C_6H_3OH$) with Donors[a]

			Dioxane		Benzophenone		Acetophenone		Azobenzene		ETC		Nitromethane	
R_1	R_2	ν	K	$\Delta\nu/\nu$	K	$\Delta\nu/\nu$	K	$\Delta\nu/\nu$	K	$\Delta\nu/\nu$	K	$\Delta\nu/\nu$	K	$\Delta\nu/\nu$
H	H	3610	4.0	65.10	7.7	48.5	8.0	51.3	1.0	65.1	1.1	44.3	1.9	16.6
H	2-*i*-Pr	3612	6.3	62.3	4.4	44.3	6.6	48.7	0.5	69.2	0.5	48.5	1.2	18.0
H	2-*t*-Bu	3610	3.7	62.3	2.9	44.3	3.0	48.5	1.0	65.1	1.1	45.7	1.1	18.0
2-Me	6-*t*-Bu	3615	1.3	48.4	2.5	29.1	2.8	30.4	0.5	47.0	0.6	36.0	1.0	15.2
2-*i*-Pr	6-*i*-Pr	3620	1.3	38.7	0.4	26.2	1.1	26.2	0.4	38.7	0.1	16.6	0.5	11.1
2-*t*-Bu	6-*t*-Bu	3645	0.9	35.7	0.3	20.6	0.3	19.2	<0.1	...	<0.1	...	0.1	9.6

[a] The equilibrium constant, K, is at 25° and is in l. mole^{-1}; ν is the OH stretching frequency in cm^{-1}; the $\Delta\nu/\nu$ values have been multiplied by 10^3; ETC stands for ethylenetrithiocarbonate; solvent is CCl_4.

Table II. Hydrogen Bonding of Hindered Alcohols ($R_1R_2R_3COH$) with Donors[a]

				Dioxane		Benzophenone		Acetophenone		Azobenzene		ETC		Nitromethane	
R_1	R_2	R_3	ν	K	$\Delta\nu/\nu$	K	$\Delta\nu/\nu$	K	$\Delta\nu/\nu$	K	$\Delta\nu/\nu$	K	$\Delta\nu/\nu$	K	$\Delta\nu/\nu$
H	*t*-Bu	*t*-Bu	3650	0.8	30.1	1.8	21.9	1.8	23.3	0.6	35.6	0.8	27.4	0.4	12.3
C_2H_5	*i*-Pr	*i*-Pr	3625	0.7	28.1	0.6	17.1	0.7	16.6	1.0	4.1	1.0	2.8	0.5	2.8
i-Pr	*t*-Bu	*t*-Bu	3635	0.5	23.4	0.4	13.8	0.2	12.4	0.6	5.9	0.7	2.8	0.2	2.5

[a] All the footnotes of Table I apply to this table also.

The data in Table III show that although the equilibrium constants of hydrogen bonding of sterically hindered phenols with tetrahydrofuran decrease with increase in the bulk of substituents, the enthalpies of hydrogen bonding are quite large. These results establish that the low equilibrium constants are mainly due to entropy factors. The $\Delta\nu_{\mathrm{OH}}$ in these systems decrease markedly with increase in the steric hindrance to the OH group and are not proportional to the enthalpy of hydrogen bonding. It is interesting that the enthalpy of hydrogen bonding is quite large for sterically hindered phenols, including the extreme case of 2,6-di-*t*-butylphenol.[11] If one were to consider $\Delta\nu_{\mathrm{OH}}$ as a measure of hydrogen bond energy, some of the more sterically hindered phenols like 2,6-diisopropyl- and 2,6-di-*t*-butylphenols would be considered as poor acceptors (proton donors) forming weak hydrogen bonds.

Table III. Hydrogen Bonding Data on Hindered Phenols ($R_1R_2C_6H_3OH$) with Tetrahydrofuran[a]

R_1	R_2	K (25°), l. mole^{-1}	$-\Delta H°$, kcal mole^{-1}	$(\Delta\nu/\nu)$ × 10^3
H	H	13.6	4.0	78.9
H	2-*i*-Pr[b]	8.0	5.0	76.2
H	2-*t*-Bu[b]	7.0	5.0	74.8
2-Me	6-Me	2.5	...	74.2
2-Me	6-*t*-Bu	1.7	5.0	56.7
2-*i*-Pr	6-*i*-Pr	1.8	5.0	52.5
2-*t*-Bu	6-*t*-Bu	0.5	8.0	23.3

[a] Solvent CCl_4. [b] Estimates making use of the data from the present work and ref 6.

Table IV. Hydrogen Bonding Data on Hindered Alcohols ($R_1R_2R_3COH$) with Tetrahydrofuran[a]

R_1	R_2	R_3	K (25°), l. mole^{-1}	$-\Delta H°$, kcal mole^{-1}	$(\Delta\nu/\nu)$ × 10^3
H	*t*-Bu	*t*-Bu	0.7	2.6	39.7
C_2H_5	*i*-Pr	*i*-Pr	0.5	2.2	33.9
i-Pr	*t*-Bu	*t*-Bu[b]	0.3	1.8	27.5

[a] Solvent CCl_4. [b] The $-\Delta H°$ value for hydrogen bonding with dioxane has been found to be 2.8 kcal mole^{-1} in cyclohexane solvent, by Dr. E. D. Becker of Naional Institutes of Health, Bethesda, Md. This enthalpy value compares well with that of methanol or *t*-butyl alcohol with dioxane (~ -2.8 kcal mole^{-1}).[19]

Quantitative thermodynamic data for sterically hindered alcohols with tetrahydrofuran and dioxane are shown in Table IV. It can be seen that just as in sterically hindered phenols, the equilibrium constants are considerably lower due to steric effects while the enthalpy is not very much altered by the bulk of the substituents. The $\Delta\nu_{\mathrm{OH}}$ again decreases with increase in the bulk of the substituents.

The absence of any relation between $\Delta\nu_{\mathrm{OH}}$ and $\Delta H°$ for the hydrogen bonding of sterically hindered phenols and alcohols with donors is not unexpected. In fact it has been found that $\Delta H°$ is linear with respect to $\Delta\nu_{\mathrm{OH}}$ only for the interaction of one acceptor with different donors.[7] For different hydroxy compounds although $\Delta\nu_{\mathrm{OH}}$–$\Delta H°$ relations may be linear, the slopes differ markedly from one hydroxy compound to another for the same set of donors.[7,12] Thus, for the same set of donors, methanol, *t*-butyl alcohol, phenol, and pentachlorophenol give different linear $\Delta\nu_{\mathrm{OH}}$–$\Delta H°$ relations. Since in the studies of Bellamy[5,6] as well as in the present work the interaction of one donor with various acceptors have been studied, one should not compare the $\Delta\nu_{\mathrm{OH}}$ of one hydroxy compound with that of the other.

The progressive decrease of $\Delta\nu_{\mathrm{OH}}$ with the increase in steric hindrance to the OH group is noteworthy. It should be pointed out that $\Delta\nu_{\mathrm{OH}}$ is not strictly proportional to $\Delta H°$, but is related to the magnitude of the splitting of the vibrational levels or the barrier height in the double minimum potential. Generally, the lower

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(11) The large value of $\Delta H°$ for 2,6-di-*t*-butylphenol may also include contributions from increased van der Waals interactions between the *t*-butyl groups and the metthylene groups of tetrahydrofuran. The authors are thankful to one of the referees for this suggestion.

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the barrier height, the greater is the energy of the hydrogen bond X–H···Y, since a decrease in barrier height is accompanied by a lowering of $R_{X\cdots Y}$. $\Delta\nu_{XH}$ also increases with a decrease in the barrier height and generally in related systems one finds a linearity between $\Delta\nu_{XH}$ and $\Delta H°$ because both $\Delta\nu_{XH}$ and $R_{X\cdots Y}$ (or the force constant) vary proportionally. Thus, in short hydrogen bonds where the barrier height is small, $\Delta\nu_{XH}$ as well as $\Delta H°$ is large. It is, however, possible to conceive of a situation where the barrier height (and $\Delta\nu_{XH}$) varies accompanied by little or no variation of $R_{X\cdots Y}$ (and $\Delta H°$). If the barrier height increases while the $R_{X\cdots Y}$ decreases slightly, then we shall have a case where increase in $\Delta H°$ will be accompanied by decrease in $\Delta\nu_{OH}$. Such instances are seen in these hindered alcohols and phenols. The decrease in $\Delta\nu_{OH}$ in these systems with increase in $\Delta H°$ can be interpreted as due to an increase in the energy of activation for proton transfer in hydrogen bonding. If this is the case, one may expect a relation between $\Delta\nu_{OH}$ and the $\Delta F°$ of the equilibria. In fact, it is found that there is a fairly linear relation between $\Delta\nu_{OH}$ and $\Delta F°$ in different O–H···O systems with a variety of hydroxylic compounds as acceptors, even though there is no simple $\Delta\nu_{OH}$–$\Delta H°$ relation. In all such systems, an increase in the enthalpy term is compensated by a decrease in the entropy term in the free-energy expression. Even in sterically hindered phenols, where in the extreme cases there may be no coplanarity of the OH group, $\Delta\nu_{OH}$ and $\Delta F°$ seem to vary proportionally.

Hydrogen bonding data of a few *para*-substituted 2,6-di-*t*-butylphenols with tetrahydrofuran are summarized in Table V. The substituent constants (σ values) of Hammett[13] have also been listed. It can be seen that neither the equilibrium constants nor the $\Delta\nu_{OH}$ values vary linearly with the substituent constants. No correlation of these data was possible with the pK_a values or the substituent constants proposed by Cohen[14] for use with 2,6-di-*t*-butylphenol. It is however interesting to note that the pK_a and the OH stretching frequencies in the infrared can be correlated with the substituent constants.[15]

Table V. Hydrogen Bonding Data of *para*-Substituted 2,6-Di-*t*-butylphenols with Tetrahydrofuran[a]

para substituent	ν	pK_a[b]	σ[c]	σ[b]	K(25°), l. mole^{-1}	($\Delta\nu/\nu$) × 10^3
t-C_4H_9	3649	14.75	−0.20	−0.14	0.5	22.0
CH_3	3649	14.77	−0.17	−0.15	...	28.8[d]
H	3645	14.22	0.00	0.0	0.5	23.3
$COOC_2H_5$	3636	11.20	0.68	0.64	1.1	26.1
CN	3632	10.15	1.00	0.88	1.3	28.9
CHO	3620	9.33	1.13	1.04	0.8	23.4
NO_2	3626	7.49	1.27	1.24	1.3	27.6

[a] Solvent CCl_4. [b] See ref 14. [c] Se ref 13. [d] See ref 5.

Unlike the hindered phenols, *para*-substituted phenols have been found to show linear relations of equilibrium constants and $\Delta\nu_{OH}$ with substituent constants.[7] The absence of the linear free energy relationship in *para*-substituted 2,6-di-*t*-butylphenols may be taken as due to steric effects in the formation of hydrogen bonded complexes. Since that OH group of 2,6-di-*t*-butylphenol is suspected to be noncoplanar,[5,6] it is likely that in the formation of the more nonplanar hydrogen bonded complexes with donors, the transmission of electrical effects by *para* substituents to the reaction center cannot be correlated by the subtituent constants. It has been known that when large steric effects are operative in transition states, the linear free energy relationships fail.[16] The linearity of pK_a with the *para*-substituent constants[14] presents a different situation since the electrical effects of substituents on the anions will play a part in this case. The linearity of the OH stretching frequencies[15] with substituent constants may be taken as due to some linear polar energy relationship which may operate even when the OH group is not coplanar. As far as the authors are aware there is no report in the literature where the electrical effects of *para* substituents on the rate or equilibrium constant of a sterically hindered site have been studied. It is felt that such kinetic studies involving the hydrogen bond in the transition state would yield interesting results.

Experimental Section

All the sterically hindered phenols were commercially available. The two sterically hindered alcohols 2,4-dimethyl-3-ethyl-3-pentanol and 2,2,4,4-tetramethyl-3-isopropyl-3-pentanol were prepared by the procedure reported in the literature.[17,18] The equilibrium constants, K, of hydrogen bonding, the frequency shift, $\Delta\nu_{OH}$, and the enthalpy of hydrogen bonding, $\Delta H°$, were determined by employing a Carl-Zeiss UR-10 spectrophotometer (LiF prism) and a Cary 14R spectrophotometer with variable-temperature cells. The method employed to determine the equilibrium constants was similar to that of Becker.[19] The experimental procedure and the reproducibility of results have been discussed in another communication.[7] The uncertainty in $\Delta\nu_{OH}$ was ±5 cm^{-1} and in $\Delta H°$, ±0.5 kcal mole^{-1}. The uncertainty in K is less than 10% and the variation in temperature in any one determination of K was ±1°.

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