491. *Steric Inhibition of Hydrogen-bonding in Solutions of 4-Methyl-2,6-di-t-butylphenol.*

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Low-resolution infrared spectra show that 4-methyl-2,6-di-t-butylphenol has a slight but measurable tendency to form hydrogen bonds with bases. In dilute solutions of this compound in basic solvents three species have been detected, one free and two hydrogen-bonded. The bonded species are believed to contain hydrogen atoms oriented in and out of the plane of the benzene ring.

Two peculiarities of hydroxyl stretching absorption in spectra of 2,6-di-t-alkylphenols (so-called "hindered phenols"[1]) are widely recognized. One is the high frequency, and the other is that little or no absorption attributable to self-association can be detected in concentrated solutions.[2,3] In spectra of 4-methyl-2,6-di-t-butylphenol dissolved in basic solvents a third peculiarity has been found, namely, the coexistence of one absorption attributable to free hydroxyl groups and two others attributable to hydrogen-bonded hydroxyl groups. These occur in the regions 3650, 3610—3580, and 3500—3390 cm.$^{-1}$, respectively.

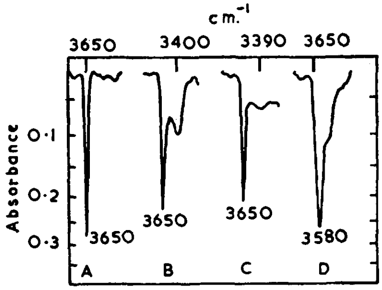

FIG. 1. *Spectra of* 0·272M-*solutions of* 4-*methyl*-2,6-*di-t-butylphenol in* (A) *cyclohexane,* (B) *diethyl ether,* (C) *triethylamine, and* (D) *dioxan. Cells* 0·1 *mm., pure solvents in reference beam.*

Solutions of this phenol in four non-basic solvents gave a single, sharp peak in the hydroxyl stretching region at approximately 3650 cm.$^{-1}$ (Table, Fig. 1A). The apparent molar absorptivity (ε_a) in each case was about 100, and Beer's law was obeyed even in the most concentrated solutions (0·5M).

Solutions in diethyl ether also gave a sharp peak at 3650 cm.$^{-1}$ which obeyed Beer's

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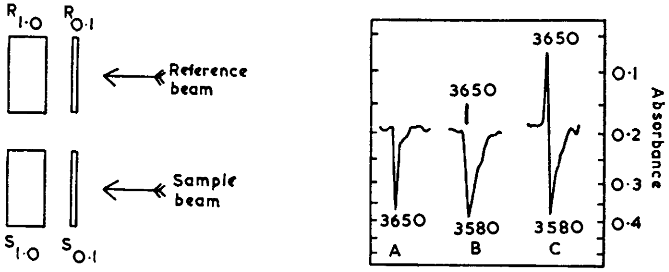
[1] Stillson, Sawyer, and Hunt, *J. Amer. Chem. Soc.*, 1945, **67**, 303.

[2] Coggeshall, *J. Amer. Chem. Soc.*, 1947, **69**, 1620; Sears and Kitchen, *J. Amer. Chem. Soc.*, 1949, **71**, 4110; Hughes, Martin, and Coggeshall, *J. Chem. Phys.*, 1956, **24**, 489; Puttnam, *J.*, 1960, 486.

[3] Bellamy and Williams, *Proc. Roy. Soc.*, 1960, *A*, **255**, 22.

law, but ε_a was only 75. As Fig. 1B shows, this peak was accompanied by a shoulder at 3600 cm.$^{-1}$ and a broad subsidiary peak at 3400 cm.$^{-1}$ which also obeyed Beer's law. Solutions in cineole and triethylamine gave similar results. Solutions in dioxan (Fig. 1D) gave superficially different spectra: shoulders at 3650 and 3400 cm.$^{-1}$ flanked a peak at 3580 cm.$^{-1}$. However, in dioxan–carbon tetrachloride (1 : 10 v/v) the main peak was at 3650 cm.$^{-1}$, with shoulders at 3580 and 3400 cm.$^{-1}$. The peaks at 3650 and 3580 cm.$^{-1}$ were successfully resolved in a differential experiment (Fig. 2).

FIG. 2. *Differential infrared spectrophotometry. Two* 0·1 *mm. cells and two* 1·0 *mm. cells* ($R_{0\cdot1}$, $S_{0\cdot1}$ *and* $R_{1\cdot0}$, $S_{1\cdot0}$, *respectively*) *were arranged as indicated, and the slit width was nominally* 60 μ. *The cells were filled as follows*:



Spectrum A. $R_{0\cdot1}$: *cyclohexane.* $R_{1\cdot0}$ *and* $S_{1\cdot0}$: *dioxan.* $S_{0\cdot1}$: 0·272M-*phenol in cyclohexane.*
Spectrum B. $R_{0\cdot1}$ *and* $R_{1\cdot0}$: *dioxan–cyclohexane* (10 : 1 v/v). $S_{0\cdot1}$ *and* $S_{1\cdot0}$: *dioxan*–0·272M-*phenol in cyclohexane* (10 : 1 v/v).
Spectrum C. $R_{0\cdot1}$: 0·272M-*phenol in cyclohexane.* $R_{1\cdot0}$: *dioxan.* $S_{0\cdot1}$ *and* $S_{1\cdot0}$: *dioxan*–0·272M-*phenol in cyclohexane* (10 : 1 v/v).

Findings for other basic solvents were qualitatively similar (see Table). Apparently the peaks found at highest frequency in direct experiments on benzene, ethyl acetate, acetonitrile, and acetone were produced by overlapping of peaks near 3650 and 3610 cm.$^{-1}$.

Hydroxyl stretching absorption in solutions of 4-*methyl*-2,6-*di*-*t*-*butylphenol.*

Solvent	Ref. 3[a]	ν (cm.$^{-1}$) Direct[b]	ν (cm.$^{-1}$) Differential[c]	ε_a[d]	Fraction not bonded[e]	
Hexane	3655	3650		101	(1·00)	(1·00)
Cyclohexane ...		3650		97	(1·00)	(1·00)
CCl_4	3650	3650		98	(1·00)	(1·00)
$CHCl_3$		3650		106	(1·00)	(1·00)
Benzene		3640	(3650), 3610, 3500			0·60
EtOAc		3620, 3480[f]	(3650), 3610, 3470[f]			0·83
MeCN	3627	3630, 3390[f]	(3650), 3610, 3390[f]			0·86
Acetone		3610, 3390[f]	(3650), 3590, 3410[f]			0·73
Et_2O	3651	3650, 3600,[f] 3400	(3650), 3600, 3400	75	0·71	0·72
Dioxan		3650,[f] 3580, 3400	(3650), 3580, 3430[f]	39	0·37	0·39
Pr^i_2O		3650, 3480	(3650), 3610, 3480	88	0·84	0·88
Cineole		3650, 3590,[f] 3400		81	0·77	
Pyridine		3650,[f] 3400	(3650), 3600,[f] 3400	31	0·30	0·29
NEt_3		3650, 3600,[f] 3390		72	0·69	

[a] ±1 cm.$^{-1}$. [b] ±10 cm.$^{-1}$. [c] ±10 cm.$^{-1}$. Solvents mixed with 1/10 vol. of cyclohexane (cf. Fig. 2). [d] From direct experiments (3650 cm.$^{-1}$). [e] First column: ε_a/105. Second column: from differential experiments. [f] Shoulder.

The peak at *ca.* 3650 cm.$^{-1}$ is attributed to the free hydroxyl group, in which the hydrogen atom lies in a t-butyl "basket," in the plane of the benzene ring.[4] From the literature[5,6] it is clear that the other peaks should be attributed to hydrogen-bonded species which, existing in dilute solutions, must be of the simple bimolecular type,

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[4] Ingold, *Canad. J. Chem.*, 1960, **38**, 1092.
[5] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, ch. 6; Sheppard in "Hydrogen Bonding," ed. Hadži, Pergamon, London, 1959, p. 85.
[6] Pimentel and McClellan, "The Hydrogen Bond," Freeman, San Francisco, 1960, ch. 3.

Phenol ··· Solvent. Only two such species can be visualized, with the hydrogen atom lying respectively in and out of the plane of the benzene ring. It is not possible to argue from known facts which frequency should be attributed to which species. The out-of-plane species lacks resonance-stabilization, but molecular models show that it is less hindered than the in-plane species.

It is interesting that, in dilute solutions in carbon tetrachloride, 2-t-butylphenols with 6-substituents smaller than t-butyl give two free-hydroxyl stretching peaks. Goddu [7] has attributed these to " in-plane " species with the hydrogen atom oriented towards the 2- or the 6-position.

Fractions representing the proportion of our phenol that is not associated with solvent at room temperature are shown in the Table. They represent the maximum proportion, because any overlap of the adjacent bands would increase the magnitude of ε_a at 3650 cm.$^{-1}$. There is good agreement between fractions from direct and differential experiments.

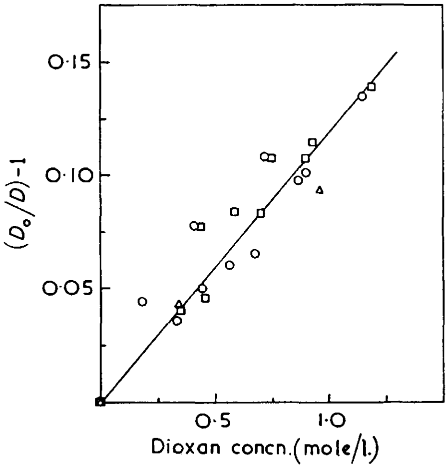

FIG. 3. *Determination of K for the equilibrium,* phenol + dioxan $\rightleftharpoons$ phenol ··· dioxan, *in carbon tetrachloride.*

□ 20°, ○ 50°, phenol 0·0242 mole/l. △ 20°, phenol 0·0454 mole/l.

The basic solvents are listed in the Table in probable order of increasing basicity.[6, 8] That this is not the order of increasing association with the phenol must be due to steric hindrance. Thus pyridine, which is less basic than triethylamine but offers less steric hindrance to hydrogen-bond formation, associates twice as much. Dioxan and cineole present an analogous contrast. Despite their great difference in basicity, diethyl ether and triethylamine associate about equally.

The equilibrium constant (K) for hydrogen-bond formation between our phenol and dioxan in dilute solutions in carbon tetrachloride has been determined at 20° and 50°. If the concentration of the phenol is relatively low, so that [dioxan] $\gg$ [phenol ··· dioxan], and if activities are assumed to be unity, K can be derived from the simple relations

$$K = \frac{[\text{phenol}\cdots\text{dioxan}]}{[\text{phenol}][\text{dioxan}]} = \frac{D_0 - D}{cD} = \frac{(D_0/D) - 1}{c},$$

where D_0 = absorbance at 3650 cm.$^{-1}$ of the phenol in CCl_4, D = absorbance at 3650 cm.$^{-1}$ of the same concentration of the phenol in CCl_4 containing dioxan, and c = concentration of dioxan.

Fig. 3 is a plot of $(D_0/D) - 1$ against c. The best straight line for the 20° points is shown ($K = 0{\cdot}12 \pm 0{\cdot}01$ l. mole^{-1}) but it is indistinguishable from that for the 50° points. Maximum values for the enthalpy and entropy change have been calculated from the

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

[8] Searles and Tamres, *J. Amer. Chem. Soc.*, 1951, **73** 3704.

extremes of the standard error; *viz.*, from $K_{293} < 0{\cdot}12 + 0{\cdot}01$ and $K_{323} > 0{\cdot}12 - 0{\cdot}01$, $-\Delta H < 1100$ cal. mole^{-1} and $-\Delta S < 8{\cdot}1$. The values of K and $-\Delta H$ are lower than any quoted by Pimentel and McClellan[9] for comparable systems. (Lindberg[10] doubted his value, $-\Delta H = 300$, for 2,6-dimethoxyphenol.)

Data in the literature[2,3] generally show no evidence that one molecule of a 2,6-di-t-alkylphenol can associate with another, but four types of association could perhaps occur, by hydrogen-bonding of in-plane and out-of-plane hydrogen atoms with electrons on oxygen atoms or benzene rings. This might explain the low frequencies found by Bellamy and Williams[3] for solid (3627 cm.$^{-1}$) and liquid 4-methyl-2,6-di-t-butylphenol (3636 cm.$^{-1}$; cf. data on acetonitrile in the Table). Spectra of 4-methoxy-2,6-di-t-butylphenol[11] show a minor, broad peak at 3450 cm.$^{-1}$ which may be attributed to hydrogen-bonding with methoxyl oxygen.

The present work establishes that this phenol can associate with sterically less hindered bases but that its tendency to associate is remarkably slight. It is apparently the first hydroxylic compound found that is not quantitatively hydrogen-bonded in dilute solutions in basic solvents. This is a phenomenon recently discovered[12] for C⋮CH compounds, and which is just revealable for t-butyl alcohol by a differential experiment.

Experimental.—4-*Methyl*-2,6-*di-t-butylphenol*. This was Eastman " Tenox " " BHT," m. p. 70·5—71° (corr.) [lit.,[1] 70° (uncorr.)]. Purity was confirmed by the full spectrum.

Solvents. Hexane and di-isopropyl ether (technical grade), chloroform and diethyl ether (" AnalaR "), and cyclohexane and carbon tetrachloride (" Spectrosol ") were used without further purification.

Benzene, ethyl acetate, acetone, and pyridine (" AnalaR ") were passed through a column of Linde molecular sieve 5A before use.

Acetonitrile was fractionally distilled from P_2O_5, K_2CO_3, and P_2O_5 in that order. 1,4-Dioxan and cineole (eucalyptol) were fractionally distilled from lithium aluminium hydride, and triethylamine from sodium.

Infrared measurements. A small, double-beam spectrophotometer with sodium chloride optics was used (Perkin–Elmer " Infracord," model 137E). The slit width was automatically controlled except in differential experiments. Measurements were carried out at 20° ±2° or 50° ± 2°. A density correction was applied for carbon tetrachloride at 50°.

Frequency readings were calibrated by using the 3655 cm.$^{-1}$ peak of the phenol in hexane[3] and the 2925 cm.$^{-1}$ peak of polystyrene, and were reproducible to ±10 cm.$^{-1}$. Absorbance readings were measured on the assumption of zero absorbance at the minimum near 3720 cm.$^{-1}$: these proved more reliable than readings measured from other baselines. Apparent molar absorptivities (ε_a l. mole^{-1} cm.$^{-1}$) were calculated from these readings.

The spectra of all solvents were checked before use, and control experiments were made as rigorously as possible.

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[9] Ref. 6, appendices B and C.

[10] Lindberg, *Soc. Sci. Fennica, Comm. Phys.-Math.*, 1957, **20**, 1.

[11] Cook, Inskeep, Rosenberg, and Curtis, *J. Amer. Chem. Soc.*, 1955, **77**, 1672; Müller and Ley, *Chem. Ber.*, 1955, **88**, 601.

[12] Wojtkowiak and Romanet, *Compt. rend.*, 1960, **250**, 3980; Brand, Eglinton, and Morman, *J.*, 1960, 2526.