

[CONTRIBUTION FROM THE CHEMICAL AND PHYSICAL RESEARCH LABORATORIES OF THE FIRESTONE TIRE & RUBBER COMPANY]

Infrared Studies of Hindered Phenols

BY WILLIAM C. SEARS AND LELAND J. KITCHEN

Infrared absorption measurements have proved¹ a useful method for studying the formation of hydrogen bonds between hydroxyl groups. Fox and Martin² observed the primary O-H bands for mono-, di- and triphenylcarbinols in the associated state at 2.97 μ , 2.89 μ and 2.87 μ , respectively. Each of these bands approached the value of 2.77 μ on extreme dilution in a non-polar solvent.

Coggeshall³ used the wave length shift between the associated and unassociated states of the hydroxyl group as a measure of the strength of the hydrogen bond formed. He classed phenols containing ortho alkyl substituents as unhindered, partially hindered or hindered on the basis of wave length shifts $\Delta\lambda > 0.15 \mu$, $0.04\mu < \Delta\lambda < 0.15 \mu$ or $\Delta\lambda < 0.04 \mu$, respectively. On this basis phenols having no or small ortho substituents were classed as unhindered phenols.

In the present investigation the primary O-H bands of twenty-nine alkyl and alkoxy phenols were studied by the dilution method. Several of the phenols were unhindered; but the others contained one or two methyl, isobornyl, *t*-butyl or *tt*-octyl groups or a combination of one of these groups with methyl, as hindering ortho substituents. Relative hindrances imparted by these groups to the hydrogen bonding of the phenol hydroxyl were determined. A hydrogen bonding index was devised in order to compare the various groups in hindering power.

Several of the compounds reported by Coggeshall³ were remeasured because he did not differentiate between the liquid and solid states. It is now found that there are large infrared shifts between the melt and solid states for several of these phenols, particularly for those without ortho substituents. Therefore a valid comparison of strengths of hydrogen bonds as determined by infrared shifts should be based on measurements on the liquid phase.

Experimental

Procedure.—Infrared bands were measured with an evacuable automatic recording spectrometer with a large sodium chloride prism, designed and constructed in the laboratories of The Firestone Tire & Rubber Co.

Wave length shifts were determined by comparing absorption bands of dilute solutions (0.07 molar solutions in carbon tetrachloride) with bands for concentrated solutions, for melts, and for crystalline solids. The concentrated solutions were prepared by wetting the phenols with just sufficient carbon tetrachloride to effect solution. Three phenols liquid at room temperature were measured without solvent. Several phenols were examined in the melted

state at temperatures slightly above their melting points; then they were allowed to crystallize and the spectra were remeasured.

The melted and crystalline samples were 0.001 in. thick compared with 0.066 in. for the dilute solutions. Thickness of the concentrated solutions varied from 0.001 to 0.002 in.

Results are summarized in Table I. Conveniently the shift of the hydroxyl band from its wave length in dilute solution to the wave length in concentrated solution is defined as $\Delta\lambda_c$; the shift from dilute solution to melt as $\Delta\lambda_m$; and the shift to the solid state, $\Delta\lambda_s$.

Values for $\Delta\lambda$ are accurate within $\pm 0.004 \mu$, while the probable error in the determination of λ is $\pm 0.02 \mu$.

In comparison with values for $\Delta\lambda_s$ which are available in the literature, the present values are intermediate between those of Coggeshall³ and those obtained by examination of the published curves of Richards and Thompson.⁴ In making these comparisons it is assumed that Coggeshall measured 4-*t*-butylphenol, 4-*t*-amylphenol and 2-*t*-butyl-4-methylphenol in the solid state. Elsewhere agreement is good except for phenol.

Materials.—The solvent was C. P. carbon tetrachloride, which was found to have no absorption in the hydroxyl region.

Most of the phenols were of analytical purity (99.0–99.9%), having been purified by recrystallization and having melting points listed in Table I. The 2,4-dimethylphenol (Eastman Kodak Co. grade) and several other liquids—2,4-dimethyl-6-*t*-butylphenol, 2,4-dimethyl-6-*tt*-octylphenol and 2,6-di-*t*-butyl-4-*s*-butylphenol—which were not purified beyond fractional distillation were about 95% pure. The 2,6-diisobornyl-4-methylphenol, which was obtained as a solid resin of b. p. 254–276° (10 mm.) and could not be purified through recrystallization, was estimated to have a purity of 70–80%.

The 2,6-dimethylphenol, 3,4,5-trimethylphenol, 2,4,6-trimethylphenol, 2,3,6-trimethylphenol and 2,3,5,6-tetramethylphenol samples were supplied through the courtesy of Shell Development Company.

Alkyl phenols containing *t*-butyl groups in the ortho position were prepared by isobutylene alkylation.⁵ The *tt*-octyl- or 1,1,3,3-tetramethylbutylphenols were prepared by alkylations with diisobutylene.⁶ The isobornylphenols were the samples which have been described.⁷ Phenol, 4-cresol, 4-*t*-amylphenol and 4-*tt*-octylphenol were obtained by recrystallization of commercial materials.

Discussion

Association in Crystalline State Compared with Liquid.—It is apparent from comparison of $\Delta\lambda_m$ and $\Delta\lambda_s$ values of Table I that the change in phase from liquid to solid cannot be neglected in

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TABLE I
 INFRARED MEASUREMENTS OF O-H BAND SHIFTS IN PHENOLS

Phenol	Melting point, °C.	λ of dil. soln., μ	Shift in O-H band in μ , dilute soln. vs. melt		
			concd. soln. $\Delta\lambda_c$	$\Delta\lambda_m$	solid $\Delta\lambda_s$
Phenol		2.75	0.261 ^a	0.249	0.365 ^b
4-Cresol		2.74	.256	.277	.297
4-Methoxyphenol	54.6-56.2	2.74	.245	.243	.190
4- <i>t</i> -Butylphenol	99.2-99.8	2.75		.200	.388 ^c
4- <i>t</i> -Amylphenol	93.7-94.1	2.76	.268	.237	.354 ^d
4- <i>t</i> -Octylphenol	85.2-85.6	2.75	.271		
3,4,5-Trimethylphenol	104.6-105.7	2.75	.259		
2,4-Dimethylphenol	20-22	2.76		.194	
2- <i>t</i> -Butyl-4-methylphenol	51.2-52.1	2.74		.081	.123 ^e
2- <i>tt</i> -Octyl-4-methylphenol	47.0-47.8	2.75	.075	.080	.094
2-Isobornyl-4-methylphenol	71.8-72.5	2.72		.156	.260
2-Isobornylphenol	77.8-78.6	2.72		.152	.258
2,6-Dimethylphenol	45.2-45.8	2.75	.085	.094	.209 ^b
2,3,6-Trimethylphenol	61.8-62.8	2.74	.053		
2,3,5,6-Tetramethylphenol	115.2-117.2	2.75	.027	.047	.154
2,4,6-Trimethylphenol	70.4-71.6	2.74	.080	.076	.235 ^f
2,4-Dimethyl-6- <i>t</i> -butylphenol	16-21	2.73		.041	
2,4-Dimethyl-6- <i>tt</i> -octylphenol		2.74	.030		
2,4-Dimethyl-6-isobornylphenol	82.9-83.0	2.75	.023	.028	.330
Bis-(2-hydroxy-3,5-dimethyl-phenyl)-isopropylmethane	160.5-161.0	2.88	.046		
2-Methyl-4,6-di- <i>t</i> -butylphenol	51.6-52.6	2.72		.034	.049 ^g
2,6-Di- <i>t</i> -butyl-4-methylphenol	69.8-70.5	2.72	.009	.007	.020 ^h
2,6-Di- <i>tt</i> -octyl-4-methylphenol	51.6-52.2	2.73	.000	.000	.010
2,6-Diisobornyl-4-methylphenol		2.72	.013		
2,4,6-Tri- <i>t</i> -butylphenol	131.0-131.2	2.71	.003		
2,6-Di- <i>t</i> -butyl-4- <i>s</i> -butylphenol		2.72	.005		
2,6-Di- <i>t</i> -butyl-4-methoxyphenol	103.7-104.7	2.72	.009		
2,6-Di- <i>t</i> -butyl-4-ethoxyphenol	83.2-84.4	2.73	.007		
2,6-Di- <i>t</i> -butyl-4-chlorophenol	79.0-79.5	2.71	.004	.004	.022

^a Literature value for $\Delta\lambda_c$, 0.181.² ^{b-i} Literature values for $\Delta\lambda_s$: ^b 0.264; ^c 0.45³ and 0.354; ^d 0.40³ and 0.334; ^e 0.334; ^f 0.324; ^g 0.123; ^h 0.184; ⁱ 0.224; ^j 0.063; ^k 0.023; ^l 0.01.³

comparing the hydrogen bonding of different phenols. Since $\Delta\lambda_s$ is greater than $\Delta\lambda_m$ for all phenols for which data were obtained, except 4-methoxyphenol, hydrogen bonding in the crystalline state appears to be stronger than in the liquid phase. On solidifying, the phenols crystallize into lattice structures in which force fields in addition to those from simple hydrogen bonding may affect the primary O-H force constant and the infrared shift. There could, for example, be a weak bond formed in crystals between the hydroxyl hydrogen atom and an aromatic carbon atom as suggested by Richards and Thompson⁴ in the case of *o*-hydroxydiphenyl. Moreover, the packing coefficient of crystalline phenols would vary with substituents in the meta and para positions. The data appear to support these conclusions as evidenced by several anomalous effects. For example, among phenols with different para substituents the difference between $\Delta\lambda_s$ and $\Delta\lambda_m$ ranged from -0.053μ to 0.188μ . Unexpectedly the $\Delta\lambda_s$ value for 2,4-dimethyl-6-isobornylphenol was greater than the corresponding value for 2-isobornylphenol, although the former has methyl instead of hydrogen in the 2-position. However, the shifts

within the liquid phase are in the expected order.

It is concluded that comparisons between different phenols of hydrogen bonding should be made on infrared shifts within the liquid phase. A study of corresponding $\Delta\lambda_c$ and $\Delta\lambda_m$ values in Table I reveals that they are essentially the same, the maximum deviation being 0.02μ . This is of interest because the $\Delta\lambda_c$ values frequently are measured more readily than the $\Delta\lambda_m$ values on unknowns to determine the positions of substituent groups.

Hydrogen Bonding Index.—The phenols without ortho substituents, being unhindered, exhibited the greatest shifts. Among the seven para substituted phenols without ortho substituents included in Table I the maximum wave length shift is about 0.267μ . The "hydrogen bonding index" is defined as the shift from dilute solution to the liquid state divided by 0.267μ . This index can assume values only between 0 for complete hindrance to hydrogen bonding and 1 for unhindered phenol. The hydrogen bonding index calculations which follow were based on the average shift $(\Delta\lambda_c + \Delta\lambda_m)/2$.

Comparison of Homologous Series.—The six para substituted phenols of Table I containing the *t*-butyl group in both ortho positions were almost completely hindered with respect to hydrogen bonding. The various para substituents had only a slight effect on hydrogen bonding, since the bonding indices for the six phenols were within the range 0.01 to 0.03.

Hydrogen bonding indices for hindered 4-methylphenols are compared in Table II. One methyl group in the ortho position decreased hydrogen bonding slightly, bringing the index down to 0.73. When both ortho positions were occupied by methyl groups, the index was 0.29, about equivalent to one *t*-butyl group (0.30) or to a *tt*-octyl group (0.29).

TABLE II

HYDROGEN BONDING INDICES^a OF HINDERED 4-METHYLPHENOLS

Ortho substituent in 2-position	Ortho substituent in 6-position				<i>tt</i> -Octyl
	Hydrogen	Methyl	Isobornyl	<i>t</i> -Butyl	
Hydrogen	1.00				
Methyl	0.73	0.29 ^b			
Isobornyl	.59 ^c	.10	0.05		
<i>t</i> -Butyl	.30	.15 ^d		0.03	
<i>tt</i> -Octyl	.29	.11			0.00

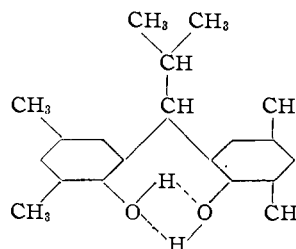
^a Index is wave length shift of O-H band from dilute soln. to liquid state divided by 0.267 μ . ^b 2,6-Dimethylphenol had an index of 0.33. ^c 2-Isobornylphenol had an index of 0.57. ^d 2-Methyl-4,6-di-*t*-butylphenol had an index of 0.13.

An ortho isobornyl group, with an index of 0.59, was between methyl and *t*-alkyl in hindrance to hydrogen bonding. However, when the isobornyl group was combined with methyl in the other ortho position, the index was 0.10, which indicated less hydrogen bonding than with a combination of methyl and *t*-alkyl in the ortho positions. The apparently anomalous increase in hindrance may be due to the bicyclic structure of the isobornyl group.

With isobornyl or *t*-alkyl groups in both ortho positions, hydrogen bonding in liquid phase approached zero, the index being 0.00–0.05, contrasted with a value of about 1.00 for the para substituted phenols without ortho substituents.

Effect of meta Substitution.—It is well known that a meta methyl group, in itself, does not hinder the phenolic hydroxyl group. However, when both ortho and meta substituents are present on adjacent carbon atoms, the meta substituent can exert a hindering effect. For example, 2,3,5,6-tetramethylphenol had an index of only 0.14 compared with indices of 0.20, 0.29 and 0.33, respectively, for 2,3,6-trimethylphenol, 2,4,6-trimethylphenol and 2,6-dimethylphenol. Apparently a meta methyl group forces an adjacent ortho methyl group closer to the hydroxyl, increasing the hindrance.

Intramolecular Hydrogen Bonding.—Evidently intramolecular association occurs between the two O-H groups of bis-(2-hydroxy-3,5-dimethylphenyl)-isopropylmethane, indicated by the fact that its O-H absorption band did not shift all the way back to the non-associated state as a result of dilution. Therefore it is concluded to be associated



Structure of Isobornylphenol.—The preparation of a monoisobornylphenol of m. p. 77.8–78.6° was described previously.⁷ Its hydrogen bonding index is 0.57, compared with 0.58 for 2-isobornyl-4-methylphenol; thus it is the ortho isomer, 2-isobornylphenol, rather than the para isomer, 4-isobornylphenol.

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Summary

Twenty-nine phenols, twenty-two of which contained methyl, *t*-butyl, *tt*-octyl and isobornyl groups as ortho substituents, were examined for degrees of hydrogen bonding by means of infrared spectroscopy. Hydrogen bonding indices were assigned to the various phenols to indicate their tendencies to associate in liquid phase. It was found that the isobornyl group, a secondary alkyl group, hindered more than methyl but less than the tertiary alkyl groups, of which *tt*-octyl hindered to a slightly greater extent than *t*-butyl.

The effect of change of phase was investigated; O-H bands for the crystalline state included anomalies such that comparisons among phenols required measurements on the liquid phase.

Methyl groups in the meta position were found to increase the hindering action of adjacent ortho methyl substituents.

An example of intramolecular hydrogen bonding with formation of an eight-membered chelation ring is pointed out.

On the basis of its observed hydrogen bonding index, a monoisobornylphenol of m. p. 77.8–78.6° was found to be 2-isobornylphenol.