THE INFRARED FREQUENCIES AND INTENSITIES OF THE HYDROXYL BAND IN ORTHO-SUBSTITUTED PHENOLS¹

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ABSTRACT

The infrared frequencies, intensities, and half-band widths of the fundamental stretching vibration of the hydroxyl group have been measured for a large number of ortho-alkyl phenols. It has been found that phenols containing a single ortho-alkyl substituent exist as cis and trans isomers in unequal amounts, the trans isomer being the more abundant. The difference in free energy between the two isomers in dilute solution in carbon tetrachloride at 24° C has been measured for ortho-cresol, 2,3-dimethyl phenol, and several ortho-tert-alkyl phenols.

INTRODUCTION

The fundamental frequencies of the hydroxyl group in o-alkyl-substituted phenols have been reported for a rather limited range of alkyl substituents by a number of workers (1, 2, 3, 4), but, with the exception of 2,6-di-t-butyl-4-substituted phenols (5), there has been no systematic study of the effect of these substituents on band intensities. The present work describes a comprehensive examination of both the frequencies and the intensities over a large range of o-alkyl substituents.

The O—H vibrational frequency, in carbon tetrachloride solution, of 2,6-di-t-butyl phenol is 36 cm⁻¹ higher than phenol (5) and since the O—H band is coplanar with the ring in both cases (5) it should therefore be possible to observe two bands in the spectra of *o*-t-butyl phenol, and perhaps in other *o*-t-alkyl phenols as well. The two bands would correspond to geometrical isomers i.e. cis and trans structures in which the O—H group points towards the alkyl substituent and away from it, respectively. These two bands were, in fact, observed in all *o*-t-alkyl phenols, and while this work was being prepared for publication Goddu (6) reported finding two bands in *o*-t-butyl phenols and in 2-t-butyl-6-methyl phenols.

The possibility of detecting geometrical isomerism in non-tertiary-alkyl-*o*-substituted phenols was also examined.

EXPERIMENTAL

A Beckman I. R. 4 spectrophotometer with lithium fluoride optics was used to measure the O—H bands, the frequencies being calibrated by the standard absorption lines of water vapor. The effective slit width was about 4 cm^{-1} . Carbon tetrachloride was employed as the solvent and solution concentrations (C) were in the range 0.01 to 0.002 molar. Three cells of thickness (l), 1, 5, and 10 mm were used. Throughout this paper the term "intensity" (A) refers to the ratio, for the substituted phenol to phenol, of the apparent integrated absorption intensities, i.e. the band areas, and numerical values of A are given relative to the intensity of phenol. The band areas were obtained from the product of the half-band width (Δv_1) and the molecular extinction coefficient $(E_{\text{max}} = (1/Cl) \log_{10} (I_0/I)v_{\text{max}})$ (7).

Many of the phenols employed were commercial products which were purified by recrystallization or distillation before use. The purity of the liquid samples was checked

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Can. J. Chem. Vol. 39 (1961)

CANADIAN JOURNAL OF CHEMISTRY. VOL. 39, 1961

by gas chromatography and some of the phenols were purified on a preparatory column. The phenols 2-t-anyl-4-methyl; 2,6-di-t-anyl-4-methyl (8); 2-t-t-octyl-4-methyl (m.p. 50-51.2°) (9);* 2,6-di-t-t-octyl-4-methyl (m.p. 53.2-54.2°) (9); 2-triethylmethyl-4methyl (m.p. 43-44°); and 2,6-di-triethylmethyl-4-methyl (m.p. 44°) were obtained by alkylation of p-cresol with the appropriate olefin by the method of Stillson, Sawyer, and Hunt (8). The hindered (2,6-substituted) and partially hindered (2-substituted) p-cresols were separated by adsorption chromatography on alumina. The yield of the last two hindered phenols was only 5 or 10%. 2-t-Butyl-5,6-dimethyl phenol (m.p. 52-53°) was obtained by alkylation of 2,3-dimethyl phenol with the theoretical amount of isobutylene. 2,6-Di-t-t-octyl-4-formyl phenol (white needles, m.p. $157-158^{\circ}$) was prepared in 25%yield from the 4-methyl derivative by oxidation with bromine (10). The main product of this reaction is a vellow crystalline material m.p. 124° C, the infrared spectrum of which suggests a para-quinolide structure (11). Since it appears to contain an equimolar quantity of HBr the analysis suggests it is 4-bromo-4-methyl-2,6-di-t-t-octyl-cyclohexadiene-2,5-one-1, hydrobromide. Analysis: Found C, 56.4; H, 8.15; Br, 32.6. Calculated for C₂₃H₄₀OBr₂: C, 56.1; H, 8.19; Br, 32.4.

2-t-t-Octyl-4-methyl-6-t-butyl phenol (m.p. 33-34°) was prepared by butylating 2-t-t-octyl-4-methyl phenol.

We are indebted to the Eastman Kodak Co. for gifts of the following phenols: 2,4,6-trisec-butyl; 2,4-di-n-amyl; 2,4,6-tri-n-amyl; 2-n-decyl-4-methyl; and 2-sec-dodecyl-4methyl.

RESULTS

It has been shown previously (5) that the frequencies of the O—H band maxima (ν_m) for 4-substituted phenols and for 4-substituted-2,6-di-t-butyl phenols can be correlated by a Hammett $\rho\sigma$ relation. Two parallel straight lines were obtained whose slopes (ρ) were both -13.7 cm^{-1} . The intensities of the two groups of substituted phenols relative to phenol and to 2,6-di-t-butyl phenol respectively can be represented on a Hammett plot by a single straight line whose slope equals 0.37 (5). The measured values of ν_m and of the intensity relative to phenol (A) for the phenols studied here have therefore been compared with the values calculated from the Hammett equation to show up any departures from the predicted values. $\Delta\nu_m$ represents the difference between the measured and calculated values of ν_m and ΔA represents the difference between the measured for an ortho substituent is the same as that for a para substituent (12). The σ values for the *t*-t-octyl and triethylmethyl groups have been assumed to be -0.19 and -0.18 respectively for structural reasons. All results are averages of at least two experiments.

The frequencies of single bands and of the main band in those phenols which show a double band are probably relatively correct to within 1 cm⁻¹.[†] Relative intensities should be correct to within about ± 0.05 . The absolute intensity of phenol obtained by graphical integration over the absorption band using log $_{10}$ (I_0/I) and applying Ramsey's correction for the wing absorption (7) has been redetermined to be 5.30 (1×10⁴ mole⁻¹ liter cm⁻²). If the band is measured only to the flat wings of the curve (13) the intensity is 4.35 in the same units. These values are in good agreement with other recent estimates (13).

The results obtained with those phenols which were substituted with at least one *t*-alkyl group in an ortho position are given in Table I. The symmetrically substituted

*The t-t-octyl group is (CH₃)₃CCH₂(CH₃)₂C---

 \dagger Frequencies given in reference 5 were low by 2 or 3 cm⁻¹ owing to an error in the spectrometer calibration.

phenols show only a single band but the asymmetrically substituted compounds show a complex band which consists of a main band at approximately the same frequency as phenol and a smaller, incompletely resolved band at a frequency approximately that of the 2,6-di-*t*-alkyl phenol. The value of $\nu_{\rm m}$ for the side band is probably correct only to 2 or 3 cm⁻¹, owing to the difficulty of separating the contribution from the main band. Typical spectra are shown in Fig. 1. Table I also includes the ratio of the intensities of the two bands (denoted by A(trans)/A(cis)).



FIG. 1. The fundamental O-H vibration bands of ortho-tert-alkyl phenols.

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The results obtained with phenols which do not contain an ortho-*t*-alkyl substituent are given in Table II.

DISCUSSION

The increases in frequency observed with 2,6-di-*t*-alkyl phenols compared with phenol are too large to be explained by the polar contributions of the *t*-alkyl groups. It has been shown previously (5) that the increase associated with 2,6-di-*t*-butyl phenols cannot be attributed to the twisting of the O—H bond out of the plane of the benzene ring. Similar evidence that the O—H bond is coplanar with the ring, or at least is nearly coplanar, has now been extended to 2,6-di-*t*-toctyl phenols.

The fundamental stretching frequency of the C==O group in substituted benzaldehydes has been shown to follow a Hammett $\rho\sigma$ relation (14). If the O—H group is coplanar in 2,6-di-*t*-alkyl-4-formyl phenols the effective σ will be the sum of $\sigma_{\text{para}}(\text{OH}) = -0.36$ plus σ_{meta} for two *t*-alkyl groups = 2×-0.12, i.e. -0.60. The shift in C==O frequency from benzaldehyde to *p*-hydroxybenzaldehyde and to 2,6-di-*t*-alkyl-4-formyl phenol should therefore be in the ratio 0.36:0.60, i.e., 3:5. If, however, the O—H bond is twisted away from the plane by the *t*-alkyl groups its effective σ will be increased i.e. become more

							A(trans)
Substituents	Σσ	cm ⁻¹	cm^{-1}	A	ΔA	<u>cm⁻¹</u>	$\frac{A(\text{trails})}{A(\text{cis})}$
Phenol	0	3612.5		1.00		18.5	
2-Bu ^r	-0.20	3607.ъ 3647.5	$\frac{-8}{32}$	0.92 0.084	0.07	18 18.5	11.0
2-Bu ^t -4-Me	-0.37	3610	-7.5	0.85	0.06	17.5	12.3
2-Bu ^t -4-MeO	-0.47	$3614 \\ 3653$	-5	0.00_9 0.79 0.05_2	0.02	17.5 17 16	13.9
2-Bu ⁴ -5-Me	-0.27	3608 3648	-8	0.86	0.04	17.5 18	9.5
2,4-Bu ₂ ^{<i>t</i>}	-0.39	3610	-8	0.86	0.09	18	11.5
2-Bu ^t -4-OH	$-0.52 \mathrm{av}$. 3616.5 3651	-3 -3	1.62/2	0.06	19	26.8/2
2,5-Bu ₂ ^{<i>t</i>} -4-OH	-0.67	3614 3652	-8	1.50/2	0.11	19 16.5	13.4 13.7
2,6-Bu ₂ ^t	-0.39	3648	30 30	$1.02^{0.10_{9}/2}$	0.17	17.5	
$2,6-Bu_2^{t}-4-Me$	-0.56	3650	29.5	0.95	0.16	19	
$4,0-BU_{2}^{*}-4-CHU$	+0.73 -0.20*	3033	30.5	1.43	0.10	17.5	
$4,4'-CH_2bis(2,6-Bu_2')$	-0.30 -0.47*	3649	$\frac{28.5}{30}$	2.40/2 2.06/2	$0.31 \\ 0.20$	19	
2-Bu ^{<i>t</i>} -6-Me	-0.37	$\frac{3617}{3640}$	-1	0.67	-0.05	17.5	4.85
2,4-Bu ₂ ^{<i>t</i>} -6-Me	-0.56	3618	-2.5	0.13_{8} 0.63	-0.03	17.5	4.85
4,4'-bis(2-Bu ^t -6-Me)	-0.28*	3616	0 22	1.54/2	-0.04	17.5 18 17	5.0
4,4'-CH ₂ bis(2-Bu ^t -6-Me)	-0.45^{*}	3618.5 2652	00.5 024	1.38/2	0.01	$\frac{17}{20}$	5.1
4,4'-Thio bis(2-Bu'-6-Me)	-0.26*	$3615 \\ 3648$	$ \begin{array}{r} 34.5 \\ -1 \\ 32 \end{array} $	0.27/2 1.62/2 0.36/2	0.1	19.5 19.5 19	4.5
2-Bu ⁺ -5,6-Me ₂	-0.44	$\begin{array}{c} 3621 \\ 3652 \end{array}$	$\frac{2}{33}$	$\begin{array}{c} 0.56 \\ 0.18_7 \end{array}$	-0.09	18.5 18	3.0
2-Am ^{<i>t</i>}	-0.19	$3608 \\ 3643$	-7 28	0.92 0.07.	0.06	$\frac{20}{21}$	12.4
2,4-Am ₂ ^t	-0.38	3609 3645	9 27	0.86	0.07	17	12.3
2-Am ^{<i>t</i>} -4-Me	-0.36	3609.5 3644	-8	0.83	0.03	17	12.4_{5}
2,6-Am ₂ ^{<i>t</i>} -4-Me	-0.55	3642.5	22.5	1.15	0.35	19.5	
2,4,6-Am ₃ ^t	-0.57	3642	21.5	1.13	0.34	20	
2-Oct ¹¹ -4-Me	-0.36	3608.5	-9	0.86	0.06	18	13.0
2.6-Oct-44-Me	-0.55	3039.5 3635 -	22 15 -	0.00_{6} 1 18	0.38	19.5	
2,6-Oct ₂ ^{<i>tt</i>} -4-CHO	+0.75	3617	14.5	$1.10 \\ 1.70$	$0.33 \\ 0.42$	20.5	
2-(C ₂ H ₅) ₃ C-4-Me	-0.35	3608	-9.5 21	0.86	0.06	17.5	13.2
$2,6-((C_2H_5)_3C)_2-4-Me$	-0.52	3635	15^{21}	1.21	0.40	18	
2-Oct ⁺⁺ -4-Me-6-Bu ⁺	-0.56	3647 (max) 3642 (center)	27 22	1.22	0.43	25.5	See text

TABLE I Frequencies and intensities of *t*-alkyl phenols

 $*\Sigma\sigma$ assigned on basis of $\nu_{\rm m}$ and A.

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positive (12, 15). The observed C=O frequencies were benzaldehyde 1710 cm⁻¹, p-hydroxybenzaldehyde 1701 cm⁻¹, 2,6-di-t-butyl-4-formyl phenol 1695 cm⁻¹ (5), and 2,6-dit-t-octyl-4-formyl phenol 1695 cm⁻¹; the frequency differences are in the ratio 9:15 in agreement with the ratio predicted for a coplanar hydroxyl group.

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Substituents	$\Sigma \sigma$	cm^{ν_m}	$\Delta \nu_{\rm m}$ cm ⁻¹	A	ΔA	$cm^{\Delta \nu_{\frac{1}{2}}}$
Phenol	0	3612.₅		1.00		18.5
3-Me	-0.07	3613.5	0	0.99	0,02	18
4-Me	-0.17	3615	0	0.94	0	17
3,4,5-Me3	-0.31	3617	0	0.90	0.01	17.5
2-Me	-0.17	3615	0	0.95	0.01	19.5
2,4-Me ₂	-0.34	3617	0	0.92	0.05	19.5
2-Me-4-Cl	+0.06	3612	0	1.08	0.06	20.5
2,4,5-Me ₃	-0.41	3618	0	0.89	0.04	19.5
2,6-Me ₂	-0.34	3622.5	5.5	0.76	-0.11	18.5
2,6-Me ₂ -4-Cl	-0.11	3618	4	0.93	-0.03	21
2,4,6-Me3	-0.51	3624.5	4.5	0.72	-0.09	18
2.3-Me ₂	-0.24	3616	0	0.94	0.03	19
2,3,5-Me ₃	-0.31	3617	0	0.90	0.02	19
2.3.6-Me ₃	-0.41	3623	5	0.75	-0.10	18
2,3,4,6-Me₄	-0.58	3625.5	5	0.69	-0.10	18
2,3,5,6-Me ₄	-0.48	3626	7	0.68	-0.14	18.5
2,3,4,5,6-Me₅	-0.65	3630	8.5	0.61	-0.15	20.5
2-Et	-0.15	3614.5	-0.5	0.97	0.03	19.5
2,6-Et ₂	-0.30	3623	6	0.84	-0.05	18
2-Pr ⁿ	-0.13	3614.5	0	0.99	0.04	19.5
2-Pr ⁿ -4-Me	-0.30	3616.5	-0.5	0.90	0.01	19
$2, 6 - \Pr_{2^{n}}$	-0.25	3621	5	-0.82	-0.09	18.5
2-Pr ⁿ -6-Me	-0.30	3623	6	0.78	-0.11	19
2-Pr ⁱ	-0.15	3614.5	-0.5	0.91	-0.03	19.5
2-Pr ⁱ -4-Me	-0.32	3616.5	-0.5	0.88	0	19
$2, 6 - \Pr_{2^{i}}$	-0.30	3623	6	0.72	-0.17	19
2-Bu ^s	-0.12	3614	0	0.89	-0.06	18.5
2,4-Bu ₂ ^s	-0.25	3616	0	0.87	-0.04	18.5
2,4,6-Bu ₃ ^s	-0.37	3622	5	0.71	-0.15	18
$2,4-Am_2^n$	-0.32	3616.5	-0.5	0.88	0	18
$2,4,6-Am_3^n$	-0.48	3622	3	0.67	-0.15	18
2-Am ⁱ	-0.23	3615.₅	-0.5	0.86	-0.06	18
2,4-Am ₂ ^s	-0.25	3615.5	-0.5	0.89	-0.02	19.5
2-n-decyl-4-Me	-0.33	3616	-1	0.88	0	19
2-sec-dodecyl-4-Me	-0.29	3615.5	1.5	0.79	-0.10	18

TABLE II Frequencies and intensities of non-tertiary alkyl phenols

Although the OH group is coplanar in the presence of strong electron-attracting groups such as CHO this does not necessarily imply that it is also coplanar when the 4-substituent is electron releasing (e.g. CH₃). However, the differences in frequency between the hydroxyl groups of the 4-methyl and 4-formyl derivatives of phenol, 2,6-di-*t*-butyl phenol, and 2,6-di-*t*-octyl phenol are 16.5 (5), 17, and 18.5 cm⁻¹ respectively compared with a calculated difference of 17.5 cm⁻¹.* That is, within the limits of experimental error the plots of $\nu_{\rm m}$ against σ for these three classes of phenols are parallel (5) and therefore the OH group has the same orientation, independent of the 4-substituent, in all cases.

The intensities of the hindered phenols give further confirmation that they are true phenols and not "pseudo" phenols containing a non-planar hydroxyl group. The intensity of phenol is two or three times as great as the intensities of alcohols (13, 16), and, therefore, since the hindered phenols have even higher intensities than phenol, they must be true phenols. Moreover, the ratio of the intensities of the 4-formyl to 4-methyl derivatives of phenol; 2,6-di-*t*-butyl phenol; and 2,6-di-*t*-t-octyl phenol are 1.66 (5), 1.51, and 1.44

*An interesting difference between the OH bands of 2,6-di-t-butyl and 2,6-di-t-t-octyl phenols is that their half-band widths appear to change in opposite directions with a change in σ (Table I) (5).

CANADIAN JOURNAL OF CHEMISTRY, VOL. 39, 1961

respectively, compared with a calculated ratio of 1.48, again suggesting that the structure of the phenols is independent of the 4-substituent.

Although the results quoted above strongly suggest that the OH group is coplanar with the ring, the accuracy of the experiments does not preclude the possibility that it is slightly twisted away from the plane. Both the resonance energy and the charge density at the carbon atom para to the resonance-inhibited group vary approximately as $\cos^2\theta$ (15, 17, 18) where θ is the angle of twist. That is, the resonance energy and charge density fall off rather slowly for small values of θ and therefore we could not detect small angles of twist in our experiments.

The conclusion that the OH group is in the plane, or at least close to it, makes the interpretation of the results obtained with single ortho-*t*-alkyl substituents comparatively straightforward. The results given in Table I and Fig. 1 clearly demonstrate the presence of two forms of *o*-*t*-alkyl phenols, as was predicted. Since the frequencies of the two bands are fairly close the one to the frequency of phenol, and the other to that of the corresponding 2,6-di-*t*-alkyl phenol, it is logical to suppose that the two forms represent geometrical isomers. The more intense band at the lower frequency will correspond to the trans isomer (T) and the less intense band at the higher frequency to the cis isomer (C).



Geometrical isomerism has been reported previously (19, 20) for *o*-substituted phenols in which the substituent can form an intramolecular hydrogen bond with the phenolic hydrogen (e.g. *o*-chlorophenol). This isomerism, which was deduced from infrared spectra, arises from the attraction of the phenolic hydrogen towards the *o*-substituent since the main band occurs at a much lower frequency than in phenol and the minor band occurs near the phenol frequency. In other words, the cis form is the most stable, whereas in *o*-*t*-alkyl phenols it is the trans form that is more stable. This suggests the presence of a steric repulsion between the phenolic hydrogen and the *t*-alkyl group, as might be expected.

Substitution of a methyl group in the 6-position increases the proportion of the isomer cis to the *t*-alkyl group. Substitution of a second methyl at the 5-position increases the proportion of the cis isomer even further, presumably because of its "buttressing" action on the methyl in the 6-position.

It should be pointed out that the occurrence of two bands does not necessarily imply that they correspond to geometrical isomers, since the low intensity band could conceivably be due to Fermi resonance (21) as has been postulated for hydroxy compounds containing the —CH₂OH group (13). This possibility can, however, be discarded since the intensity of the subsidiary (cis) band decreases slightly as the two bands get closer together on going from *o-t*-butyl to *o-t*-amyl phenol, which is contrary to what would be expected from Fermi resonance. The results obtained with 2-*t*-butyl-6-methyl phenols and with 2-*t*-butyl-5,6-dimethyl phenol would also be difficult to explain on this basis. Furthermore, the spectra of structurally similar phenols e.g. *p-t*-butyl phenol, 2,6-diethyl phenol, 2,6-di-isopropyl phenol, etc. do not show any subsidiary bands.

The difference in free energy (ΔG) between the two isomers can be calculated from the

476

477

ratio of the intensities of the trans to cis bands in an *o*-*t*-alkyl phenol. This energy difference should be independent of the presence or absence of a 4-substituent, since any change in resonance energy produced by a 4-substituent will presumably alter the depths of the two coplanar potential minima by the same amount. However, the measured ratio of the intensities should be corrected for the fact that when the O—H group is cis to the t-alkyl group, as it must be in 2,6-di-t-alkyl phenols, the intensity is higher than phenol. whereas when it is trans to the substituent the intensity probably approximately follows the Hammett equation (5) and will be lower than phenol. For example, the average calculated cis intensity for 2-t-butyl phenol (1.09) is obtained from the intensities of 2.6-di-t-butyl phenol (1.02), and 2,6-di-t-butyl-4-methyl phenol (0.95) by applying corrections for the polar effects of an o-t-butyl group $(-(-0.20 \times 0.37))$ and for the effect of an o-t-butyl group and a p-methyl group $(-(-0.20-0.17)\times 0.37)$. The calculated trans intensity is based on phenol (1.00) less the effect of an *o-t*-butyl group i.e. 0.93. For 2-t-butyl-6-methyl phenol the calculated intensity cis to the t-butyl group is based on the calculated cis intensity of o-t-butyl phenol corrected for the polar effect of the 6-methyl group, and the calculated trans intensity is based in the same way on the measured intensities of 2.6-dimethyl and 2,4,6-trimethyl phenol. The measured trans to cis intensity ratio must be multiplied by the calculated cis to trans intensity ratio in order to obtain the true relative amounts of the two isomers. Table III gives the steps in the calculations

TABLE III Cis – trans isomerism of *o*-alkyl phenols

o-Substituents	Av. calc. cis intensity	Av. calc. trans intensity	$\frac{\text{Calc.}}{A(\text{cis})}$	$\frac{Measured}{A(trans)}$	[trans] [cis]	ΔG kcal/ mole	% trans isomer	% cis isomer
$\begin{array}{c} 2\text{-Bu}^{4} \\ 2\text{-Am}^{t} \\ 2\text{-Oct}^{tt} \\ 2\text{-C}_{2}H_{5})_{3}C \\ 2\text{-Bu}^{t-6}\text{-Me} \\ 2\text{-Bu}^{t-5}\text{-6}\text{-Me}_{2} \\ 2\text{-CH}_{3} \\ 2\text{-CH}_{3} \\ 2\text{,}3\text{-}(CH_{3})_{2} \end{array}$	1.09 1.275 1.31 1.34 1.03 1.00	0.93 0.93 0.93 0.93 0.83 0.76 ₅	$ \begin{array}{r} 1.17 \\ 1.37 \\ 1.41 \\ 1.44 \\ 1.24 \\ 1.31 \\ \end{array} $	$12.3 \\ 12.4_5 \\ 13.0 \\ 13.2 \\ 4.8_5 \\ 3.00$	$14.39 \\ 17.06 \\ 18.30 \\ 19.01 \\ 6.01 \\ 3.92$	$\begin{array}{c} 1.5_{7} \\ 1.6_{7} \\ 1.7_{1} \\ 1.7_{4} \\ 1.0_{6} \\ 0.8_{0} \\ 0.5_{1} \\ 0.7_{7} \end{array}$	$\begin{array}{c} 93.5\\ 94.5\\ 94.8\\ 95.0\\ 85.7\\ 79.7\\ 70.5\\ 78.6\end{array}$	$6.5 \\ 5.5 \\ 5.2 \\ 5.0 \\ 14.3 \\ 20.3 \\ 29.5 \\ 21.4$

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of the percentage of cis and trans isomers and the difference in free energy (ΔG) in kcal/ mole between the two isomers in dilute solution in carbon tetrachloride at 24° C. ΔG is obtained in calories from the relation

$$\log_{10} \frac{[\text{trans}]}{[\text{cis}]} = \frac{\Delta G}{2.3RT} \,.$$

The measured trans/cis ratio for 2-*t*-butyl and 2-*t*-amyl have been taken from the values found for their 4-methyl derivatives; and for 2-*t*-butyl-6-methyl the ratio obtained with this phenol has been used. This was done since these compounds were known to be very pure and since the measurements were repeated at least six times, including once on a high-resolution Perkin–Elmer prism-grating spectrometer, model 112 G. Average values of the ratio for the other phenols of these types are in quite good agreement with the values chosen. The measured trans/cis ratio for 2-*t*-butyl and 2-*t*-butyl-6-methyl phenols are in good agreement with the values of Goddu (6), although our frequencies are from 3 to 8 cm⁻¹ higher than the values he reported, the differences being most pronounced for 2,6-di-*t*-butyl phenols and for the cis isomers of various *o*-*t*-butyl phenols.

CANADIAN JOURNAL OF CHEMISTRY, VOL, 39, 1961

The percentages of the cis isomers given in Table III show, as would be expected, that the cis isomer decreases as the size of the *t*-alkyl substituent is increased, but is increased by substitution of a methyl at the 6-position or by two methyls at the 5- and 6-positions.

The values of ΔG obtained for 2-t-butyl-6-methyl phenol and for 2-t-butyl-5,6dimethyl phenol can be combined with the value for 2-t-butyl phenol to give the differences in free energy between the cis and trans isomers of o-cresol and 2,3-dimethyl phenol. These values are also included in Table III. It was also possible to obtain a rough estimate of ΔG for the two forms of 2-t-t-octyl-4-methyl-6-t-butyl phenol. The OH band of this compound is asymmetric and from the degree of asymmetry observed on the prismgrating instrument ΔG was estimated to be 0.17 kcal/mole. The intensity of the band was also compared with the intensity of the combined band of mixtures of different proportions of 2,6-di-t-t-octyl-4-methyl phenol and 2,6-di-t-butyl-4-methyl phenol. A value of ΔG of 0.30 kcal/mole was obtained in this way. These values are in reasonably good agreement with the value of 0.14 kcal/mole obtained by difference from 2-t-t-octyl and 2-t-butyl phenol.

The ratio of the intensities of the cis to trans isomers of *o*-chlorophenol is about 50:1 in carbon tetrachloride at room temperature (22, 23), corresponding to $\Delta G \sim 2.3$ kcal/ mole. We have found that for 2-chloro-6-methyl phenol this ratio increases to $\geq 100:1$ ($\Delta G \geq 2.7$ kcal/mole). The two values of ΔG can be combined to obtain ΔG for *o*-cresol ≥ 0.4 kcal/mole, in reasonable agreement with the value given in Table III.

The results given in Table II show that a single non-tertiary alkyl group substituted in the ortho position gives a measured increase in frequency and decrease in intensity in good agreement with the values calculated from the Hammett equation (5). However, the results given in Table III show that these phenols must exist as cis-trans isomers in unequal amounts. The only direct evidence for this is that the half-band widths $(\Delta \nu_{1})$ are definitely greater for these *o*-alkyl phenols than for phenol or for the corresponding 2,6-dialkyl phenols. This suggests the presence of two unresolved bands, particularly since the half-band widths would be expected to decrease below the value for phenol with alkyl substitution (5) (see also results for 3-methyl, 4-methyl, and 3,4,5trimethyl phenol in Table II). Failure to resolve these bands is not surprising since the band maxima would appear to be less than 10 cm⁻¹ apart in general and even the prismgrating spectrometer would not resolve the two bands of 2-*t*-*t*-octyl-4-methyl-6-*t*-butyl phenol where a separation of about 15 cm⁻¹ is expected.

The positive values of $\Delta \nu_{\rm m}$ observed with the 2,6-dialkyl phenols in Table II (and which are also encountered with 2,6-di-*t*-alkyl phenols) suggest a steric interaction between these non-tertiary alkyl groups and the hydroxyl group. On the other hand, the values of ΔA are negative for these phenols, whereas positive values were obtained with the 2,6-di-*t*alkyl phenols. This shows that the intensities cannot be simply related to the extent of steric interference by the alkyl groups. However, for the phenols listed in Table II the values of $\Delta \nu_{\rm m}$ and ΔA both tend to increase with the expected increase in steric interaction (see 2,6-dimethyl; 2,3,6-trimethyl; 2,3,4,6-tetramethyl; 2,3,5,6-tetramethyl; and pentamethyl phenol). This result cannot be due to any saturation of the electronic effects produced by the increasing number of substituents (5) since this would cause both $\Delta \nu_{\rm m}$ and ΔA to decrease. The magnitude of these differences may, however, have been reduced because of saturation effects; somewhat larger values would smooth out the curves in Fig. 2 (see below).

In Fig. 2 values of $\Delta \nu_{\rm m}$ and ΔA for 2,6-dialkyl phenols have been plotted against the values of ΔG obtained from the *o*-alkyl phenols. There is no direct justification for this



FIG. 2. Differences between measured and calculated frequencies, and intensities, of 2,6-dialkyl phenols plotted against ΔG .

procedure, but it is obvious that the values of $\nu_{\rm m}$ and A for these phenols must be related in some way to the steric interaction of the alkyl groups with the hydroxyl group, and that this is measured approximately by ΔG . Both plots apparently show a discontinuity between the methyl phenols and the *t*-alkyl phenols, the curves going through a maximum or minimum. This shows that ortho-alkyl groups have two different effects on the hydroxyl, the magnitude of the two effects varying with the size of the alkyl groups.

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A possible explanation of these results is that mild steric interaction between the alkyl and hydroxyl groups narrows the potential-energy well of the stretching mode of the O—H bond; this will increase the vibration frequency and decrease its amplitude and hence decrease the intensity. Stronger steric repulsions will begin to separate the proton from the electrons of the O—H bond since the repulsion is exerted primarily on the electrons of the phenolic hydrogen and only through them on the proton itself. This will tend to polarize the bond (i.e. $\overset{b}{O}$ — $\overset{b}{H}$) and increase the intensity, and at the same time will weaken the internal force constant and so decrease the frequency. Incidentally the values of ΔG do not increase with the size of the *t*-alkyl substituent as rapidly as might be

expected, which may be because the energy is minimized by an increase in the C— \hat{O} —H angle. This forcing of the phenolic hydrogen away from its equilibrium position, as the substituents become larger than *t*-butyl, would also tend to decrease the O—H bond strength and hence $\nu_{\rm m}$.

The frequencies of the trans isomers of *o*-*t*-alkyl phenols, which are appreciably below their calculated values, are obviously much more readily influenced by the alkyl substituent than are the intensities (cf. small values of ΔA for these phenols in Table I); i.e. the intensities, but not the frequencies, follow the usual Hammett $\rho\sigma$ relations. The low frequencies observed must mean that an *o*-*t*-alkyl substituent has an effect on the hydroxyl group even when the latter is pointing away from it. This effect might be due to a more rigid geometry in the trans isomer compared to phenol (5). An alternative explanation that appears to be more consistent with the results is that *t*-alkyl groups exert van der Waals attraction on the lone pairs of electrons on the oxygen. This withdrawal of electrons from the oxygen would be transmitted to the O—H bond, the

CANADIAN JOURNAL OF CHEMISTRY, VOL. 39, 1961

frequency of which would be decreased. This suggestion helps to explain why $\Delta \nu_{\rm m}$ is higher for the cis isomer of o-t-alkyl phenols than for the corresponding 2,6-di-t-alkyl phenol. In the cis isomer the only effect on the hydroxyl is one of steric repulsion, whereas in di-t-alkyl phenols there is also the attraction of the oxygen's electrons by the second *t*-alkyl group, which will decrease the frequency. The same effect may also be operating in ortho halophenols since the frequency, in carbon tetrachloride solution, of the trans isomer decreases by 5 cm^{-1} on increasing the size of the substituent from bromine to iodine, whereas the corresponding decrease for these two para-substituted phenols is only 1 cm⁻¹ (22, 23).

An o-methyl or 2,3-dimethyl group has no effect, other than the calculated polar effect, on the frequency of the trans isomer (Table II). Therefore in 2-t-butyl-6-methyl and in 2-t-butyl-5,6-dimethyl phenol $\Delta \nu_{\rm m}$ for the cis (to t-butyl) isomer has about the same value as for 2-*t*-butyl phenols (Table I). On the other hand, $\Delta \nu_{\rm m}$ values for the trans (to *t*-butyl) isomers of these phenols are below $\Delta \nu_{\rm m}$ values for 2,6-dimethyl and 2,3,5,6-tetramethyl phenol because of the influence of the t-butyl group. Non-tertiary alkyl groups in the ortho position apparently, therefore, only affect the hydroxyl group when it points towards them.

The barrier to rotation of the hydroxyl group in 2,4,6-tri-t-butyl phenol has been estimated from dielectric measurements to be 2.8 kcal/mole (24). The rotational barrier in this compound will be lower than in phenol owing to steric repulsion by the t-butyl groups (~ 1.6 kcal/mole) and also, perhaps, to a decrease in the resonance interaction between the hydroxyl and the ring because of the polar effects of the alkyl substituents. The barrier in phenol is, therefore, ≥ 4.4 kcal/mole.

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REFERENCES

P. J. KRUEGER and H. W. THOMPSON. Proc. Roy. Soc. (London), A, 250, 22 (1959).
W. C. SEARS and L. J. KITCHEN. J. Am. Chem. Soc. 71, 4110 (1949).
L. J. BELLAMY and R. L. WILLIAMS. Proc. Roy. Soc. (London), A, 254, 119 (1960).

- L. J. BELLAMY and R. L. WILLIAMS. N. A. PUTTNAM. J. Chem. Soc. 486 3.
 - Ind R. L. WILLIAMS. Proc. Ro J. Chem. Soc. 486 (1960). Can. J. Chem. 38, 1092 (1960)
 - K. U. Ingold.
 - R. F. GODDU. J. Am. Chem. Soc. 82, 4533 (1960)
- D. A. RAMSAY. J. Am. Chem. Soc. 74, 72 (1952).
 G. H. STILLSON, D. W. SAWYER, and C. K. HUNT.
 L. J. KITCHEN. J. Am. Chem. Soc. 70, 1290 (1948). J. Am. Chem. Soc. 67, 303 (1945).
- 10. L. A. COHEN. . Org. Chem. 22, 1333 (1957
- E. MÜLLER and K. LEY. Chem. Ber. 88, 601 (1955). 11.
- E. M. TAFT. Steric effects in organic chemistry. John Wiley & Sons, Inc., New York. 1956. Chap. 13. T. D. FLYNN, R. L. WERNER, and B. M. GRAHAM. Australian J. Chem. 12, 575 (1959). 12. R. W. TAFT.
- 13.

- H. D. PERRN, R. L. WERNER, and D. M. OKARAM. Instituting J. Chem. 12, 979 (1955).
 H. W. THOMPSON, R. W. NEEDHAM, and D. JAMESON. Spectrochim. Acta, 9, 208 (1957).
 R. W. TAFT and H. D. EVANS. J. Chem. Phys. 27, 1427 (1957).
 R. MOCCIA and H. W. THOMPSON. Proc. Roy. Soc. (London), A, 243, 154 (1957).
 C. A. COULSON. Conference on quantum mechanical methods in valence theory. U.S. Govt. Printing Office. 1951, p. 47.

 - B. E. G. MCRAE and L. GOODMAN. J. Mol. Spectroscopy, 2, 464 (1958).
 19. O. R. WULF, U. LIDDEL, and S. B. HENDRICKS. J. Am. Chem. Soc. 58, 2287 (1936).
 20. L. PAULING. J. Am. Chem. Soc. 58, 94 (1936).
 21. E. FERMI. Z. Physik, 71, 250 (1931).
 22. G. ROSSMY, W. LÜTTKE, and R. MECKE. J. Chem. Phys. 21, 1606 (1953).
 23. A. W. PLUTKE, L. Am. Chem. Soc. 59, 2508 (1088).
- G. ROSSMY, W. LÜTTKE, and R. MECKE. J. Chem. Phys. 21, 1606 (1953).
 A. W. BAKER. J. Am. Chem. Soc. 80, 3598 (1958).
 M. DAVIES and R. J. MEAKINS. J. Chem. Phys. 26, 1584 (1957).

480

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- James K. Harper, Jennifer A. Doebbler, Elisabeth Jacques, David M. Grant, Robert B. Von Dreele. 2010. A Combined Solid-State NMR and Synchrotron X-ray Diffraction Powder Study on the Structure of the Antioxidant (+)-Catechin 4.5-hydrate. *Journal of the American Chemical Society* 132, 2928-2937. [CrossRef]
- Riccardo Amorati, Stefano Menichetti, Elisabetta Mileo, Gian Franco Pedulli, Caterina Viglianisi. 2009. Hydrogen-Atom Transfer Reactions from ortho -Alkoxy-Substituted Phenols: An Experimental Approach. *Chemistry - A European Journal* 15:10.1002/chem.v15:17, 4402-4410. [CrossRef]
- Elizabeth M. Heider, James K. Harper, David M. Grant, Angela Hoffman, Frank Dugan, David P. Tomer, Kim L. O'Neill. 2006. Exploring unusual antioxidant activity in a benzoic acid derivative: a proposed mechanism for citrinin. *Tetrahedron* 62, 1199-1208. [CrossRef]
- 5. N. I. Garbuz, Yu. A. Sokolov, L. P. Solovei, R. P. Litvinovskaya, S. V. Drach, A. V. Baranovskii, V. A. Khripach. 2005. IR Spectroscopic Investigation and Conformational Analysis of Unsaturated C20 and C22 Steroid Alcohols. *Journal of Applied Spectroscopy* **72**, 334-343. [CrossRef]
- 6. A Welzel, A Hellweg, I Merke, W Stahl. 2002. Structural and Torsional Properties of o-Cresol and o-Cresol-OD as Obtained from Microwave Spectroscopy and ab Initio Calculations. *Journal of Molecular Spectroscopy* 215, 58-65. [CrossRef]
- Grzegorz Litwinienko, Elzbieta Megiel, Marcin Wojnicz. 2002. Hydrogen Bonding between Phenols and Fatty Acid Esters: 1 H NMR Study and ab Initio Calculations. Organic Letters 4, 2425-2428. [CrossRef]
- 8. Yasukazu Ohkatsu, Takeshi Nishiyama. 2000. Phenolic antioxidants-effect of ortho-substituents. *Polymer Degradation and Stability* 67, 313-318. [CrossRef]
- 9. Bert T.G. Lutz, Marcel H. Langoor, John H. van der Maas. 1998. The sensorial potentials of the OH-stretching mode: phenols. Vibrational Spectroscopy 18, 111-121. [CrossRef]
- Noriko Noguchi, Yoshihide Iwaki, Mareyuki Takahashi, Erika Komuro, Yoshiaki Kato, Kunio Tamura, Osamu Cynshi, Tatsuhiko Kodama, Etsuo Niki. 1997. 2,3-Dihydro-5-hydroxy-2,2-dipentyl-4,6-di-tert-butylbenzofuran: Design and Evaluation as a Novel Radical-Scavenging Antioxidant against Lipid Peroxidation. Archives of Biochemistry and Biophysics 342, 236-243. [CrossRef]
- Marcus Brewster, Emil Pop, Ming-Ju Huang, Nicholas Bodor. 1994. Rotational barriers in phenol and sterically congested phenol derivatives, an AM1 study. *Journal of Molecular Structure: THEOCHEM* 303, 25-38. [CrossRef]
- 12. Marcus E. Brewster, Ming-Ju Huang, Emil Pop, Nicholas Bodor. 1993. Hydroxyl stretching in substituted phenols: An AM1 study. *International Journal of Quantum Chemistry* **48**:10.1002/qua.v48:20+, 7-15. [CrossRef]
- 13. E.T.G. Lutz, J.H. van der Maas. 1983. Structural information from OH-stretching vibrations—XIII. Bandshape and bandmaximum of phenols in CCl4 and CS2. Spectrochimica Acta Part A: Molecular Spectroscopy 39, 1007-1011. [CrossRef]
- J.A. Faniran, H.F. Shurvell. 1982. Vibrational spectra of mesidine and mesitol. Spectrochimica Acta Part A: Molecular Spectroscopy 38, 1155-1162. [CrossRef]
- 15. Yasukazu Ohkatsu, Tohru Haruna, Tetsuo Osa. 1977. Kinetic Evaluation of Reactivity of Phenolic Derivatives as Antioxidants for Polypropylene. *Journal of Macromolecular Science: Part A Chemistry* 11, 1975-1988. [CrossRef]
- 16. M. Simonyi, I. Kovács, J. Kardos, S. Holly. 1976. Determination of the equilibrium constant of hydrogen bonding between substituted h-[d]-phenols and vinyl acetate in CCl4 by i.r. measurements. Spectrochimica Acta Part A: Molecular Spectroscopy 32, 1387-1392. [CrossRef]
- 17. M. Simonyi, I. Kovács, J. Kardos, S. Holly. 1975. "Steric" absorption peak in the infrared spectra of 2,6-diisopropylphenols. *Tetrahedron Letters* 16, 1631-1632. [CrossRef]
- H. Pivcová, L. Jiráčková, J. Pospíšil. 1973. Antioxidants and stabilizers. XLIII. Structure of phenolic antioxidants and infrared spectra of the hydroxyl groups. *Journal of Polymer Science: Polymer Symposia* 40, 283-295. [CrossRef]
- W.A. Seth-Paul, A. Van Duyse. 1972. A new substituent constant derived from carbonyl stretching frequencies of simple R'R"CO molecules. Spectrochimica Acta Part A: Molecular Spectroscopy 28, 211-234. [CrossRef]
- J.H.S. Green, D.J. Harrison, W. Kynaston. 1972. Vibrational spectra of benzene derivatives—XV. Spectrochimica Acta Part A: Molecular Spectroscopy 28, 33-44. [CrossRef]
- J.H.S. Green, D.J. Harrison, W. Kynaston. 1971. Vibrational spectra of benzene derivatives—XIV. Spectrochimica Acta Part A: Molecular Spectroscopy 27, 2199-2217. [CrossRef]

- 22. M. Simonyi, F. Tüdős The Hydrogen Atom Abstraction Reaction from O-H Bonds 127-183. [CrossRef]
- 23. REFERENCES**Books are referred to by numbers under 100, while papers from 100 onward 397-410. [CrossRef]
- 24. A. M. de Roos. 1968. The carbonyl stretching vibration of substituted benzophenones. *Recueil des Travaux Chimiques des Pays-Bas* 87, 1359-1367. [CrossRef]
- 25. M. Horak, E.R. Lippincott, R.K. Khanna. 1967. Molecular conformation and vibrational spectra of p-halogeno derivatives of anisole. *Spectrochimica Acta Part A: Molecular Spectroscopy* 23, 1111-1119. [CrossRef]
- 26. G. Durocher, C. Sandorfy. 1967. A study of the effects of solvent on overtone frequencies. *Journal of Molecular Spectroscopy* 22, 347-359. [CrossRef]
- 27. D. Neerinck, L. Lamberts. 1966. Chaleurs D'Interaction de Complexes par Liaison Hydrogène. 1. Complexes Alcool ou Phénol
 Pyridine. Bulletin des Sociétés Chimiques Belges 75, 473-483. [CrossRef]
- 28. J. A. Howard, K. U. Ingold. 1965. THE KINETICS OF THE INHIBITED AUTOXIDATION OF TETRALIN. II. Canadian Journal of Chemistry 43:10, 2724-2728. [Abstract] [PDF] [PDF Plus]
- 29. A. W. BAKER, A. T. SHULGIN. 1965. Preferred Repulsive Interaction: a Novel Halogen–Hydroxyl Interaction. *Nature* 206, 712-713. [CrossRef]
- A.W. Baker, H.O. Kerlinger, A.T. Shulgin. 1964. The hydroxyl stretching bands of phenols: some aspects of half-band widths. Spectrochimica Acta 20, 1477-1486. [CrossRef]
- 31. A.W. Baker, A.T. Shulgin. 1964. Conformers of o-cis-propenyl phenols. Spectrochimica Acta 20, 153-158. [CrossRef]
- 32. J. A. Howard, K. U. Ingold. 1963. THE INHIBITED AUTOXIDATION OF STYRENE: PART III. THE RELATIVE INHIBITING EFFICIENCIES OF ORTHO-ALKYL PHENOLS. *Canadian Journal of Chemistry* 41:11, 2800-2806. [Abstract] [PDF] [PDF Plus]
- A. ASHFORD, C. J. SHARPE, F. F. STEPHENS. 1963. Thymol Basic Ethers and Related Compounds: Central Nervous System Depressant Action. *Nature* 197, 969-971. [CrossRef]
- I. Brown, G. Eglinton, M. Martin-Smith. 1962. Infra-red studies with substituted ortho-bromophenols—I. Spectrochimica Acta 18, 1593-1602. [CrossRef]