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"STERIC" ABSORPTION PEAK IN THE INFRARED SPECTRA OF 2,6-DIISOPROPYLPHENOLS

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Summary: The so far unreported 3641 cm^{-1} absorption of 2,6-i.Pr_2-phenols is assigned to a particular conformation of the rotating i.Pr groups.

The absorption of the O-H fundamental stretching vibration of phenols unsubstituted or substituted by n.alkyl groups in the ortho position appears in CCl_4 solution at frequencies lower than 3620 cm^{-1} in the infrared spectrum[1,2]. The absorption peak is shifted towards frequencies higher than 3640 cm^{-1} for 2,6-t.Bu_2-phenols[1,3,4]. The IR spectrum of 2-t.Bu-substituted phenols shows two absorption peaks[4]. The phenomenon is commonly interpreted by the reasonable assumption that the O-H group of phenols is coplanar with the aromatic ring owing to slightly hindered rotation, hence in 2-t.Bu-phenol the O-H is either cis or trans to the substituent thus giving rise to two different absorptions at 3647 cm^{-1} and 3608 cm^{-1}, respectively. The presence of cis and trans isomers could be observed even in cases when the 6-position of 2-t.Bu-phenol was substituted by methyl group[4]. Cis absorption has also been observed for other 2-t.alkyl substitutions[4].

The cis absorption cannot be detected for 2-isopropylphenol. Surprisingly, however, two absorption peaks appear in the spectra of 2,6-i.Pr_2-phenols. (Earlier papers reported one absorption around 3620 cm^{-1} in CCl_4 solution[3,4,5].) We found that both peaks remained after careful purifications. On addition of slightly polar solvent (vinyl acetate) to CCl_4 solutions of 2,6-i.Pr_2-phenols, the intensity of both absorption peaks decreases owing to hydrogen bond formation while the ratio of intensities of the two peaks remains essentially constant (Table). Consequently, both peaks indicate free O-H absorptions. The origin of the 3641 cm^{-1} peak is suggested to be the steric interaction of O-H and i.Pr groups. The strength of this interaction depends strongly on the actual conformation

Table. Infrared spectral data for 2,6-i.Pr$_2$-phenols at 45°C.

Compound	ν_{O-H} in CCl_4 cm^{-1}		$\frac{I_{3619}}{I_{3641}}$ in CCl_4	$\frac{I_{3619}}{I_{3641}}$ in vinyl acetate-CCl_4 mixtures
2,6-i.Pr$_2$-phenol	3619	3641	7,8 ± 1,0	6,4 ± 1,0
2,6,2',6'-i.Pr$_4$-dian*	3619	3641	6,5 ± 1,0	6,8 ± 1,0

*dian= 4,4'-isopropylidene-bisphenol

of the i.Pr group. The interaction is strong when the O-H is captured between the two methyls of the i.Pr group, and the 3641 cm^{-1} peak can be assigned to this particular conformation[6]. The interaction between i.Pr and O-H groups resembles in this conformation to that of t.Bu and O-H groups. In other possible rotational conformations of the i.Pr group, however, the interaction is weak between O-H and the ortho substituent which then resembles to an ethyl group. The two absorptions observed are therefore the consequence of rotating ortho-i.Pr groups existing in different conformations.

The term "steric" peak for the 3641 cm^{-1} absorption seems reasonable. This term may also be extended to "cis" peaks in cases of unsymmetrically substituted ortho-t.alkylphenols.

REFERENCES

1. D. S. Davies, H. L. Goldsmith, A. K. Gupta and G. R. Lester: J.Chem.Soc. 4926 (1956)
2. K. U. Ingold: Can.J.Chem. 38, 1092 (1960)
3. L. J. Bellamy and R. L. Williams: Proc.Roy.Soc. A254, 119 (1960)
4. K. U. Ingold and D. R. Taylor: Can.J.Chem. 39, 471 (1961)
5. S. Singh and C. N. R. Rao: J.Amer.Chem.Soc. 88, 2142 (1966)
6. The statistical weight of this conformation in 2-i.Pr-phenol is too small to be observable; the preference of the O-H to be faced to the free 6-position over the substituted 2-position can be estimated to be 5:1