

Hydrogen Bonding in Phenols. IV. Intramolecular OH... π Hydrogen Bonds of Some Alkyl Derivatives of Dihydroxydiphenyl-methane, -sulfide, -disulfide, -selenide

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Infrared spectroscopy reveals abnormally strong intramolecular OH... π hydrogen bonds in 2,2'-dihydroxy-3,3'-di-*t*-butyl-5,5'-dimethyl derivatives of diphenylmethane, diphenylsulfide, diphenyldisulfide and diphenylselenide.

Strong intramolecular OH...O hydrogen bonds are reported in compounds having the hydrogen bond incorporated in a conjugated system as *e.g.* in *o*-substituted phenols *etc.* [1–4]. Since intramolecular OH... π hydrogen bonds are less encountered [5], intermolecular OH... π hydrogen bonds (charge-transfer complexes) are much more investigated [6].

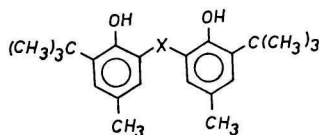
In our previous papers [4, 7] the possible formation of a strong intramolecular OH... π hydrogen bond in 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane has been mentioned.

Present investigation is directed towards the problem of the stereochemistry of intramolecular association through hydrogen bonds of such novolacs where both aromatic nuclei are bonded through methylene (*I*), sulfur (*II*), two sulfurs (*III*) and selenium (*IV*) bridges.

Experimental

Infrared spectra were recorded with a Unicam SP 100 G spectrophotometer in the 3100–3650 cm⁻¹ region in carbon tetrachloride and chloroform solutions. The calibration was checked against the spectrum of water after each group of measurements. Frequency measurements for the free and intrabonded OH are believed to be accurate to ± 1 cm⁻¹.

Analar carbon tetrachloride was used without further purification. Analar chloroform was dried several times by passage through a column of blue silica gel before direct use. All samples were of chromatographic purity [8]. These compounds were studied as follows:



X = —CH ₂ —	2,2'-dihydroxy-3,3'-di- <i>t</i> -butyl-5,5'-dimethyldiphenylmethane (<i>I</i>)
X = —S—	2,2'-dihydroxy-3,3'-di- <i>t</i> -butyl-5,5'-dimethyldiphenylsulfide (<i>II</i>)
X = —S—S—	2,2'-dihydroxy-3,3'-di- <i>t</i> -butyl-5,5'-dimethyldiphenyldisulfide (<i>III</i>)
X = —Se—	2,2'-dihydroxy-3,3'-di- <i>t</i> -butyl-5,5'-dimethyldiphenylselenide (<i>IV</i>)
	2,6-di- <i>t</i> -butyl-4-methylphenol (<i>V</i>)

Results and Discussion

Infrared spectral data of the compounds studied are listed in Tables 1 and 2.

In our previous papers [4, 7], we reported infrared spectra of two novolac type polyphenols. Our results showed that in carbon tetrachloride these compounds assume well-defined conformations involving the OH...OH and OH... π intramolecular and intermolecular hydrogen bonds.

Infrared spectral data listed in Tables 1 and 2 show that intramolecular hydrogen bond is present in all compounds studied since the molar absorptivities of bands assigned to the $\nu(\text{OH})$ -bonded are concentration independent.

Compounds *I*, *II*, *IV* display two absorption bands in the 3416–3504 cm⁻¹ region (in CCl₄) which we assign to the O—H... π intramolecular hydrogen bonds. Support for this assignment is adduced from the fact that the OH... π bond is facilitated by the enhanced proton acceptor nature of both aromatic nuclei resulting from the electron releasing alkyl groups (*t*-butyl and methyl groups). In spite of the fact that the ionization potential values (*I*_D) of the compounds studied are unknown, it is possible those to be compared with ionization potential value of

Table 1

OH...H Bond frequencies of bis(alkylphenyl)dihydroxy compounds in CCl₄

Com- pound	Conc. [mM]	Cell thickness [mm]	$\nu(\text{OH})$								
			free			bonded					
			ν	$\Delta\nu_{1/2}$	ϵ^a	ν	$\Delta\nu_{1/2}$	ϵ^a	ν	$\Delta\nu_{1/2}$	ϵ^a
<i>I</i>	100	0.2	3624	30	105	3446	—	100	3504	75	215
	50	0.47	3623	29	105	3444	—	110	3506	75	220
	10	0.96	3624	30	105	3444	—	105	3504	78	215
	1	9.93	3623	30	105	3446	—	105	3504	70	220
<i>II</i>	100	0.1	—	—	—	3418	70	150	3500	—	75
	50	0.47	—	—	—	3419	70	150	3500	—	75
	10	0.96	—	—	—	3419	73	150	3501	—	70
	1	9.93	—	—	—	3416	68	150	3501	—	75
<i>III</i>	100	0.1	—	—	—	3439	39	230	—	—	—
	10	0.96	—	—	—	3438	39	225	—	—	—
	5	9.93	—	—	—	3439	38	230	—	—	—
<i>IV</i>	100	0.1	—	—	—	3416	70	125	3488	—	80
	50	0.47	—	—	—	3416	77	125	3490	—	85
	10	0.96	—	—	—	3416	70	120	3488	—	80
	1	9.93	—	—	—	3418	70	130	3490	—	80
<i>V</i>	50	0.2	3642	15	240	—	—	—	—	—	—

ν and $\Delta\nu_{1/2}$ given in cm⁻¹, ϵ^a in l mole⁻¹ cm⁻¹; compound *V* is listed for comparison purposes.

Table 2

OH...H Bond frequencies of bis(alkylphenyl)dihydroxy compounds in CHCl_3

Com- pound	Conc. [mM]	Cell thickness [mm]	$\nu(\text{OH})$								
			free			bonded					
			ν	$\Delta\nu_{1/2}$	ε^a	ν	$\Delta\nu_{1/2}$	ε^a	ν	$\Delta\nu_{1/2}$	ε^a
I	100	0.1	3616	32	110	3432	—	110	3506	—	100
	70	0.47	3620	31	125	3436	—	120	3506	—	110
	50	0.47	3619	34	125	3440	—	120	3506	—	110
	35	0.96	3620	36	130	3440	—	125	3503	—	115
	10	0.96	3621	—	135	3442	—	125	3504	—	115
II	100	0.1	—	—	—	3420	81	130	3490	—	60
	70	0.47	—	—	—	3422	81	130	3490	—	60
	50	0.47	—	—	—	3422	80	120	3490	—	65
	35	0.96	—	—	—	3420	82	130	3490	—	65
	10	0.96	—	—	—	3420	82	140	3490	—	65
III	100	0.1	—	—	—	3440	50	190	—	—	—
	70	0.47	—	—	—	3440	55	190	—	—	—
	50	0.47	—	—	—	3440	51	200	—	—	—
	35	0.96	—	—	—	3440	60	190	—	—	—
	10	0.96	—	—	—	3440	58	190	—	—	—
IV	100	0.1	3616	—	—	3418	110	120	3480	—	—
	70	0.47	3616	—	—	3420	120	120	3480	—	—
	50	0.47	3616	—	—	3420	115	130	3485	—	—
	35	0.96	3617	—	—	3420	110	125	3480	—	—
V	50	0.2	3636	10	180	—	—	—	—	—	—

 ν and $\Delta\nu_{1/2}$ given in cm^{-1} , ε^a in $\text{l mole}^{-1} \text{cm}^{-1}$.

hexamethylbenzene ($I_D = 8.15 \text{ eV}$) [6], because six methyl groups of this compound are opposed, *e.g.* in compound I, with one *t*-butyl, methyl, and methylene group each.

As it follows from the paper by *Szczepaniak* and *Tramer* [6], the decreasing value of ionization potential in a series of compounds: benzene \rightarrow hexamethylbenzene, results in an increase of frequency differences ($\Delta\nu$) between free OH group (ν_0) and bonded OH groups (ν) of phenol in a mixture with the above-mentioned hydrocarbons (in CCl_4):

	benzene	hexamethylbenzene
I_D	9.56 eV	8.15 eV
$\Delta\nu$	30 cm^{-1}	105 cm^{-1}

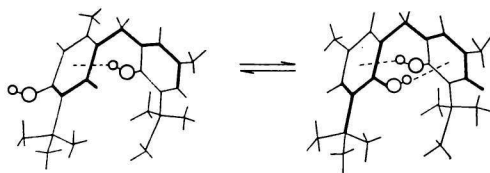
where the $\Delta\nu$ of compound I was observed to be 110 cm^{-1} (Table 1).

When comparing infrared spectral data of 2,2'-dihydroxy-4,4'-dimethyldiphenylmethane [7] with those of 2,2'-dihydroxy-3,3'-di-*t*-butyl-5,5'-dimethyldiphenylmethane (I), great differences in the nature of hydrogen bonds become evident. Thus, the former compound displays a strong intermolecular hydrogen bond ($\nu(\text{OH})$, $3292 \rightarrow 3326 \text{ cm}^{-1}$), intramolecular hydrogen bond ($\nu(\text{OH})$ at 3486 cm^{-1}) and free OH group ($\nu(\text{OH})$ at 3608 cm^{-1}). Compound I does not reveal any intermolecular

hydrogen bond; nevertheless, free OH groups ($\nu(\text{OH})$ at 3623 cm^{-1}) and intramolecular hydrogen bond at 3444 and 3504 cm^{-1} are seen in its spectrum. These differences in nature of the hydrogen bonds of the compounds in question can be explained by steric factors as reported by Cairns and Eglinton [5], i.e. the bulky *t*-butyl groups in *o*-position to the phenolic group prevent intermolecular association.

Even 2,6-di-*t*-butyl-4-methylphenol (*V*) exhibits due to the steric hindrance, much weaker intermolecular hydrogen bond e.g. with nitriles in CCl_4 (ΔH 1.1 kcal/mole) [9] as compared with that of phenol (ΔH 4.3 kcal/mole) [1]. This fact can be associated with the steric effect of two *t*-butyl groups attached in *o*-positions to the phenolic group.

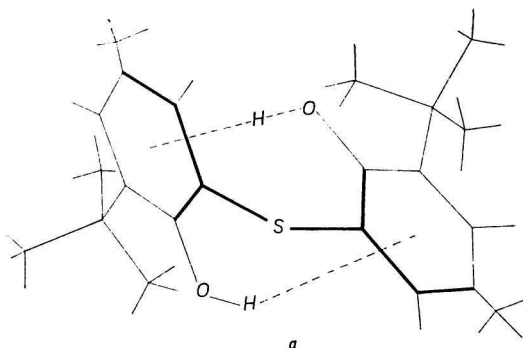
The presence of two bands belonging to OH groups involved in intramolecular hydrogen bond in compounds *I*, *II*, *IV* can be most likely ascribed to two different the $\text{OH}\dots\pi$ bonds resulting from the two conformers present in equilibrium:



This presumption is in accordance with the fact that the stretching frequencies of OH group involved in the intermolecular hydrogen bonding of 2,2'-dihydroxy-4,4'-dimethyldiphenylmethane [7] ($\nu(\text{OH})$ $3292 \rightarrow 3326\text{ cm}^{-1}$) differ to a small extent only from those involved in the intramolecular $\text{OH}\dots\text{O}$ hydrogen bond of a tetranuclear novolac [4, 7] ($\nu(\text{OH})$, 3255 cm^{-1}).

Dreiding models of the compounds examined (Fig. 1a, b) suggest that the interacting groups (OH and π -electrons of the aromatic nuclei) can approach each other up to $\sim 3.0\text{ \AA}$, which is a suitable distance for the intramolecular hydrogen bonding.

It is worth noting that compound *III* (Table 1, Fig. 1) displays one band at 3439 cm^{-1} in CCl_4 only thereby suggesting the presence only one type of intramole-



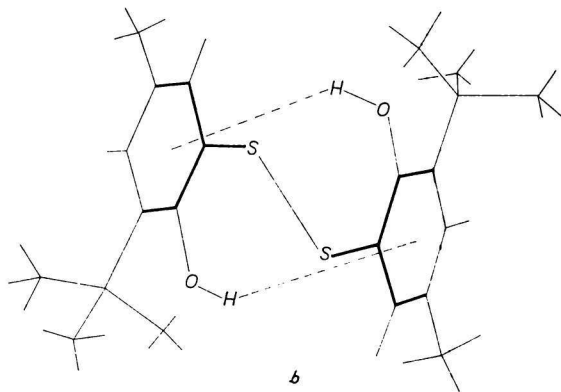


Fig. 1. Dreiding models of 2,2'-dihydroxy-3,3'-di-*t*-butyl-5,5'-dimethyldiphenylsulfide (a) and 2,2'-dihydroxy-3,3'-di-*t*-butyl-5,5'-dimethyldiphenyldisulfide (b).

cular OH... π hydrogen bond. This phenomenon most likely due to two atoms of sulfur between the aromatic nuclei, results in preventing the OH... π bonds to affect each other, as known with compounds *I*, *II*, *IV*.

Relatively close values of the stretching frequencies of the OH intramolecularly bonded of all compounds studied, exclude the possibility an intramolecular S...H—O hydrogen bonding formation with compound *II*. Furthermore, the presumption that the concentration independent band at 3444 cm⁻¹ in the spectrum of compound *I* would belong to the OH...O bonds eliminates the presence of bands in compounds *II* and *IV*, because in such a case bands due to free OH groups, as in substance *I*, should be seen in the spectrum.

As can be seen from Table 2, the stretching frequencies of OH free and OH bonded (in CHCl₃) differ only slightly from those taken in CCl₄ what indicates that hydroxyl groups are sterically hindered against the molecules of solvent.

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References

1. *The Hydrogen Bond*. (G. C. Pimentel and A. L. McClellan, Editors.) P. 47. W. H. Freeman, San Francisco, 1960.
2. Brooks C. J. W., Eglinton G., Morman J. F., *J. Chem. Soc.* **1961**, 106, 661.
3. Kováč Š., *Chem. Zvesti* **17**, 475 (1963).
4. Bennet W. S., Eglinton G., Kováč Š., *Nature* **214**, 776 (1967).
5. Cairns T., Eglinton G., *J. Chem. Soc.* **1967**, 5906.
6. Szczepaniak K., Tramer A., *J. Phys. Chem.* **71**, 3035 (1967).
7. Kováč Š., Eglinton G., *Tetrahedron* **25**, 3599 (1969).
8. Korček Š., Holotík Š., Leško J., Veselý V., *Chem. Zvesti* **23**, 281 (1969).
9. Lopes S. C. M., Thompson H. W., *Spectrochim. Acta* **24A**, 1367 (1968).

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