

Intramolecular hydrogen bond in alkylene- and thiodiphenols

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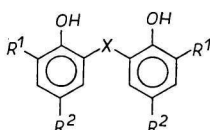
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The region of the hydroxyl stretching frequencies in alkylene- and thiodiphenols was investigated. The concentration dependence of the wavenumbers and of the molar extinction coefficients was taken as the basis for the identification of the type of hydrogen bond in the individual molecules. The results are discussed from the point of view of the presence of the individual conformational forms.

Besides the sharp absorption band corresponding to the stretching vibration of the free hydroxyl group, the i.r. spectra of alkylenediphenols display another one or more bands, belonging to the vibrations of the associated hydroxyl groups [1]. The sharp band of the free OH group sometimes disappears in the presence of a bulky alkyl substituent located in the positions *ortho* to the hydroxyl groups. A similar situation can be observed also in 2,2'-thiodiphenols [2, 3]. Since the above-mentioned compounds contain more than one proton acceptor in their molecules they represent a mixture of conformers with the hydroxyl group free or bound in the intramolecular hydrogen bond or, eventually, a mixture of conformers involving two types of the weak intramolecular hydrogen bond.

The derivatives of alkylene- and thiodiphenols are known as oxidation inhibitors of organic materials. Their antioxidative effect depends largely on the kind of substituents on the phenolic nuclei and on the kind of linking bridge [4, 5].



Scheme 1

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
R ¹	H	H	H	CH ₃	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₈ H ₁₇	CH ₃ C ₆ H ₁₀	C ₆ H ₅ (CH ₃)CH	OCH ₃	<i>t</i> -C ₄ H ₉	H
R ²	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	<i>t</i> -C ₈ H ₁₇
X	CH ₂	C(CH ₃) ₂	S	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	C(CH ₃) ₂	S

We studied the region of wavenumbers and the concentration dependences of the stretching vibrations of hydroxyl groups in the compounds shown in Scheme 1.

On the basis of the obtained results and literature data the occurrence of the individual conformational forms with regard to the type of the weak intramolecular hydrogen bond is discussed.

Table 1
Infrared spectral data of the hydroxyl groups in alkylene- and thiodiphenols

Com- pound	Con- centra- tion ^a Cell	Free OH group		Intramolecular hydrogen bond OH...π			Intramolecular hydrogen bond OH...O			Intermolecular hydrogen bond OH...O	
		$\bar{\nu}^b$	$\Delta\bar{\nu}^c$	ϵ^d	$\bar{\nu}^b$	ϵ^d	$\bar{\nu}^b$	ϵ^d	$\bar{\nu}^b$	ϵ^d	
I	1	3611	27	15	—	3461	56	3280	285		
	2	3612	23	19	—	3461	55	3280	170		
	3	3611	23	34	—	3461	64	3281	161		
	4	3611	22	65	—	3460	76	3279	117		
	5	3611	24	83	—	3461	87	3279	84		
II	1	3616	24	20	3509	3419	140 ^e	—	—		
	2	3616	24	22	3510	3419	147	—	—		
	3	3615	25	26	3509	3420	148	—	—		
	4	3619	24	23	3509	3419	150	—	—		
	5	3616	24	21	3507	3417	151	—	—		
III	1	3610	36	22	3521	3461 ^f	100	3340	66		
	2	3609	36	30	3520	3460	109	3341	53		
	3	3610	33	34	3520	3460	106	3341	29		
	4	3610	32	42	3521	3461	121	3341	9		
	5	3611	35	40	3521	3461	115	3343	6		
IV	3	3618	29	46	3522	3471	57	3343	14		
	4	3618	28	44	3521	3471	53	3343	10		
	5	3619	29	44	3522	3471	51	3340	3		
	1	3633	19	65	3516	3454	91	—	—		
	2	3631	19	67	3515	3453	89	—	—		
V	3	3633	19	67	3516	3454	86	—	—		
	4	3613	19	72	3516	3454	93	—	—		
	5	3633	20	73	3516	3454	97	—	—		
	3	3619	43	42	3509	3440	48	—	—		
	4	3620	40	32	3509	3440	35	—	—		
5	3621	41	32	3511	3441	39	—	—			

Table 1 (Continued)

VII	1	3628	29	58	3511	168	3450	72	—	
	2	3628	29	64	3512	197	3450	82	—	
	3	3629	29	68	3513	196	3450	85	—	
	4	3628	29	68	3511	208	3450	85	—	
	5	3626	28	73	3511	220	3450	90	—	
VIII	1	3619	—	—	3520	146	3450	153	—	
	2	3618	—	—	3520	152	3450	163	—	
	3	3618	—	19	3520	147	3450	157	—	
	4	3619	—	21	3519	154	3449	164	—	
	5	3618	—	—	3522	152	3452	160	—	
IX	3	—	—	—	3558 ^{e,g}	140	3470	7	—	
	4	—	—	—	3560	156	3469	8	—	
	5	—	—	—	3561	161	3471	10	—	
	1	—	—	—	3480 ^e	1480	—	—	—	
	2	—	—	—	3481	1487	—	—	—	
X	3	—	—	—	3481	1449	—	—	—	
	4	—	—	—	3481	1497	—	—	—	
	5	—	—	—	3482	1444	—	—	—	
	1	3611	38	38	3523	54	3457 ^f	101	3342	
	2	3611	38	46	3524	55	3456	95	3342	
XI	3	3611	35	56	3523	57	3456	87	3342	
	4	3611	38	65	3524	62	3457	87	3344	
	5	3612	39	64	3524	62	3457	85	3344	
	1	0.2 mol l ⁻¹ , 0.271 mm;	2. 0.1 mol l ⁻¹ , 0.402 mm;	3. 0.04 mol l ⁻¹ , 1.03 mm;	4. 0.01 mol l ⁻¹ , 3.99 mm;	5. 0.04 mol l ⁻¹ , 10.35 mm.				
	2	0.2 mol l ⁻¹ , 0.271 mm;	2. 0.1 mol l ⁻¹ , 0.402 mm;	3. 0.04 mol l ⁻¹ , 1.03 mm;	4. 0.01 mol l ⁻¹ , 3.99 mm;	5. 0.04 mol l ⁻¹ , 10.35 mm.				

a) 1. 0.2 mol l⁻¹, 0.271 mm; 2. 0.1 mol l⁻¹, 0.402 mm; 3. 0.04 mol l⁻¹, 1.03 mm; 4. 0.01 mol l⁻¹, 3.99 mm; 5. 0.04 mol l⁻¹, 10.35 mm.

b) in cm⁻¹; c) in cm⁻¹; d) in 1 mol⁻¹ cm⁻¹; e) values of $\Delta\bar{\nu}_i$ [cm⁻¹] in the order of decreasing concentrations: 70, 64, 65, 65, 65 for the compound II; 34, 37, 38 for the compound IX and 38, 37, 37, 37, 34 for the compound X; f) intramolecular hydrogen bond OH...S; g) intramolecular hydrogen bond OH...OCH₃.

Experimental

The studied compounds (Table 1) were synthesized by the usual methods and purified to the constant melting or boiling points. Their physicochemical constants were in agreement with the literature data.

The infrared absorption spectra in the region 2900–3650 cm^{-1} were measured on a Unicam SP 100G spectrophotometer in tetrachloromethane using NaCl cells. The polystyrene foil served as a calibration standard. The reading accuracy of the positions of the absorption bands corresponding to the stretching vibrations of the free OH groups and of those bound in an intramolecular hydrogen bond was $\pm 1 \text{ cm}^{-1}$. In the case of intermolecular hydrogen bonds the reading accuracy was $\pm 5 \text{ cm}^{-1}$. The used tetrachloromethane was spectrally pure.

Results and discussion

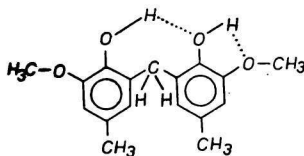
Compounds *I*–*III* differ in the kind of the bridge joining the two phenolic nuclei. Compound *I* was thoroughly studied by several authors [6, 7] who assigned the sharp band at 3611 cm^{-1} to the free hydroxyl group, the band at 3461 cm^{-1} to the hydroxyl group bound by an intramolecular OH...O hydrogen bond and the broad band at about 3200 cm^{-1} (Table 1) to a hydroxyl group bound by an intermolecular hydrogen bond (dimer). The possibility of the formation of an intramolecular hydrogen bond of OH... π type is excluded since, e.g. the wavenumber of the stretching vibration of the hydroxyl group bound by an intramolecular hydrogen bond in 2-benzyl-4-methylphenol is 3564 cm^{-1} [8]. In the latter case the presence of an OH... π bond is evident. The situation changes considerably when the methylene bridge is replaced by the isopropylidene one. First of all, compound *II* does not show the tendency to associate (the absence of the band around 3300 cm^{-1}) even at the concentration of 0.2 M. This is surprising since the steric effect of the two hydroxyl groups comes from one side only and also 2-*tert*-butyl-4-methylphenol shows the tendency to associate [9]. Since also compound *I* forms only dimers with the cyclic structure [7], in the case of compound *II* the steric effect of the two methyl groups in the alkylene bridge hinders the formation of the dimer. Additionally, the i.r. spectrum of the compound *II* displays two bands of a hydroxyl group bound by an intramolecular hydrogen bond (concentration-independent bands at 3509 and 3419 cm^{-1}). The band at 3419 cm^{-1} can be obviously assigned to a conformer involving the OH...OH type of intramolecular hydrogen bond. This is confirmed by the presence of the free hydroxyl band at 3616 cm^{-1} , shifted by 5 cm^{-1} to higher wavenumbers owing to the steric effect. The band at 3509 cm^{-1} is ascribed to a conformer with two intramolecular OH... π hydrogen bonds, similarly as is the case with compound *X* [1]. The formation of such conformation can be explained by steric effects of two methyl groups present in the bridge linking the two phenolic nuclei. The i.r. spectrum of the compound *III* with the sulfur bridge displays four absorption bands in the region 3300–3650 cm^{-1} . The concentration-dependent band at 3340 cm^{-1} corresponds to the conformation with an intermolecular hydrogen bond. With regard to the concentration independence of the vibration wavenumber the formation of a cyclic dimer can be assumed, similarly as it is in the compound *I*. The band at 3521 cm^{-1} is ascribed to a conformation with an intramolecular hydrogen bond of the OH... π type, similarly as is the case with compound *II*. Discussable remains the significance of the band at 3461 cm^{-1} . In comparison with compound *I* it seems that it could be assigned to the OH...OH hydrogen bond although some authors [2, 10] ascribe the same band in 2,2'-thiodiphenol and its derivatives to

the bond of the OH...S type. Similarly *Mertes* [11, 12] reports that the band at 3453 cm^{-1} in 7-phenyl-1,4-oxothio-spiro[4,5]-7-decanol can be explained by the presence of the bond of the OH...S type. Thus it seems more probable that the discussed bond in the compound *III* is of the OH...S type. Support for this assumption is adduced from the presence of the band at 3461 cm^{-1} also in the spectrum of 2,2'-dithio(3-*tert*-butyl-5-methylphenol) [3] wherein, owing to the great distance of the oxygen atoms, the formation of an OH...OH bond can be excluded. The same situation as with compound *III*, but with slightly shifted bands, is also in the compound *XI*.

Going further to di(3-*tert*-butyl-5-methylphenols) having strongly shielded hydroxyl groups the situation changes. Compounds *V* and *IX*, similarly as 2,2'-thiodi(3-*tert*-butyl-4-methylphenol) [3], do not associate (the absence of the band at about 3300 cm^{-1}). The reason for this behaviour is the steric hindrance caused by the presence of substituents in positions *ortho* to the OH groups [1]. In the sequence 2-benzyl-4-methylphenol, 2-(α -methylbenzyl) and 2-(α,α -dimethylbenzyl)-4-methylphenol the strength of intramolecular hydrogen bond increases and the wavenumber of the corresponding band changes from 3564 through 3544 to 3530 cm^{-1} [8]. In the same order increases the strength of an OH... π bond in alkylenedi(3-*tert*-butyl-5-methylphenols). Accordingly, the only absorption band observed in the spectrum of the compound *X* can be ascribed to a conformation with two hydrogen bonds of the OH... π type [1]. The *tert*-butyl substituent located in the *ortho* positions to the hydroxyls (compare compounds *I* and *IV*) causes the twisting out of the phenolic nuclei forming thus a "trans configuration" (see [6]). In the case of this conformation the conditions are favourable for the formation of an OH... π bond. A comparison of the compounds *II* and *X* shows that the presence of *tert*-butyl substituent in one *ortho* position and the isopropylidene bridge represent such steric hindrance that the formation of an OH...O bond becomes impossible and the corresponding absorption band is no more observed in the spectrum.

By comparing the compound *III* and 2,2'-thiodi(3-*tert*-butyl-4-methylphenol) [3, 10] it becomes clear that the steric hindrance of the hydroxyl groups in the 6,6' positions in the compounds with sulfur bridge causes disappearance of the absorption band of the free hydroxyl group. Apparently, the latter compound represents an equilibrium mixture of conformers involving intramolecular OH... π and OH...S bonds.

The effect of the substituent in the positions 6,6' in the series of methylene di(4-methylphenols) can be seen in the compounds *I*, *IV*–*IX*. The relatively small methyl substituent is unable to hinder the formation of the dimer (occurrence of the band at 3343 cm^{-1}). As already discussed for *tert*-butyl, the bulky substituents, such as *tert*-octyl, methylcyclohexyl, as well as α -methylbenzyl, hinder the association in a similar way. Very close values of the stretching vibrations corresponding to the hydroxyl groups involved in an intramolecular hydrogen bond indicate the similar steric effects of these substituents. It is interesting that the spectrum of the compound *VIII* displays the band of the free



Scheme 2

hydroxyl group, similarly as is the case with spectrum of 2,6-di(α -methylbenzyl)-4-methylphenol [8]. In the spectrum of the latter compound the free hydroxyl group can be identified by the presence of a shoulder in the region of 3619 cm^{-1} . The intramolecular OH... π hydrogen bond is more easily formed with the more basic proton acceptor, which, in the above compound, is a polysubstituted phenolic nucleus. In the case of compound IX an intramolecular hydrogen bond is preferentially formed whereby the oxygen of the methoxy group acts as a proton acceptor of the π -electron base. This fact is supported by the presence of the band at 3558 cm^{-1} which can be compared with the band at 3557 cm^{-1} in *ortho* methoxyphenol [13]. In the similar compound (IV) the corresponding band can be found at 3522 cm^{-1} (Table 1). Compound IX, which does not exhibit the band of the free phenolic group, has probably the structure shown in Scheme 2. Obviously, the ring size determines the strength of the above type of the intramolecular hydrogen bond. While in the strained five-membered ring only a weak hydrogen bond is formed (band at 3558 cm^{-1}), in the eight-membered one the bond is stronger (band at 3471 cm^{-1}).

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