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## The Structure and Configuration of Dihydroxydiphenyl Sulfides Derived from Alkylcresols by Infrared Spectra

BY JOHN L. BINDER, JOSEPH C. AMBELANG AND FRED J. WEBB

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Infrared spectra show that *o,o'*-dihydroxydiphenyl sulfides exist partly in the *cis* and partly in the *trans* configuration whereas crystalline sulfides derived from 2,5-dialkylphenols have the *p,p'*-dihydroxydiphenyl sulfide structure. Evidence is presented for the formation of OH---S bonds.

### Introduction

Several years ago two of the authors<sup>1</sup> described the configuration of dihydroxydiphenylmethanes as deduced from studies of the OH band shift in the infrared region of the spectrum. When the occasion arose to prepare a similar set of compounds in which the central alkylidene group was replaced by a sulfur atom, it seemed desirable to study also the OH bands to determine the spatial configurations of the molecules and the effect of replacing the alkylidene group with a sulfur atom. These measurements are reported here.

### Experimental

(a) **Preparations. Sulfides.**—The general method is illustrated. Melting points and analyses are shown in Table I.

**Di-(4-hydroxy-2-methyl-5-*tt*-octylphenyl) Sulfide (II).**—One-half mole (110 g.) of 6-*tt*-octyl-3-methylphenol was dissolved in 300 ml. of hexane and cooled to 0–5°. One-fourth mole (25 g.) of sulfur dichloride in 100 ml. of hexane was dropped into the first solution with stirring over a period of 35 min. The stirring was continued as the orange-yellow solid which formed at first was replaced by near-colorless crystals. After stirring vigorously with 200 ml. of water, the solid was filtered off, slurried with sodium bicarbonate solution, filtered and washed with water, and then petroleum ether until colorless. The air dried yield weighed 45.3 g. The product was purified by repeated recrystallizations from a hexane-heptane mixture.

**Di-(2-hydroxy-3,5-di-*t*-butyl-6-methylphenyl) Disulfide (VIII).**—A solution of 0.06 mole (14.4 g.) of sodium sulfide monohydrate and 2 g. of sulfur was prepared by refluxing in 75 ml. of ethanol. To the hot solution was added 0.1 mole (28.5 g.) of 2-bromo-4,6-di-*t*-butyl-3-methylphenol. The resulting solution was refluxed for 5 hr. and allowed to stand overnight. By cooling and fractional precipitation by addition of water there was isolated 8.2 g. of crude sulfide melting in the range 126–139°. Two recrystallizations from ethanol gave a constant melting point.

The mixed melting point was not lowered upon admixture with the disulfide isolated as one of the constituents from the reaction product of 2-methyl-4,6-di-*t*-butylphenol with sulfur monochloride. The reaction was carried out as described by Albert,<sup>2</sup> with care to keep the temperature below 85° after removal of solvent. By fractional crystallization<sup>3</sup> from ethanol 13.8% disulfide was isolated along with 30.0% of monosulfide.

**Methyl 2-Mercaptobenzoate (IX).**—Technical grade 2-mercaptobenzoic acid was recrystallized from 100 parts of boiling water and esterified according to the directions of Gattermann.<sup>4</sup> The product was washed with water and aqueous sodium bicarbonate before distillation.

**Methyl 2-Methylthiobenzoate (X).**—Technical 2-mercaptobenzoic acid was methylated by the method described in the patent literature.<sup>5</sup> The steam distilled product was recrystallized to constant melting point from 84% aqueous methanol and dried *in vacuo* at 56°.

**2-Hydroxyphenyl methyl sulfide (XIII)** was prepared according to the method of Holt and Reid.<sup>6</sup>

(b) **Infrared Spectra.**—The infrared spectra of the compounds studied were obtained in 0.05 *M*<sup>7a</sup> CCl<sub>4</sub> solutions, and in mulls and melts using a Beckman IR2 spectrophotometer as well as, for some compounds, a Beckman DK2 spectrophotometer. The latter was especially useful in resolving bands which appeared only as weak shoulders on very much stronger bands in the IR2 spectra. The wave lengths given are accurate to 0.01  $\mu$ . The results of the measurements of the wave lengths of the OH bands for the compounds studied are given in Table II. It was impossible to obtain spectra in concentrated solutions because of the limited solubility of these compounds in CCl<sub>4</sub>.

In view of the conclusions reached regarding the assignments of these bands attempts were made to find evidence of OH---S bonding in other compounds. Thus the spectra of 2-hydroxyphenyl methyl sulfide, methyl 2-mercaptobenzoate, methyl 2-methylthiobenzoate and di-(2-hydroxy-3,5-di-*t*-butyl-6-methylphenyl) disulfide in the OH region were obtained. These results are given in Tables III and in Table II.

### Discussion

The spectra of sulfides I, II, III in Table II have only one band at 2.75  $\mu$  in dilute solutions but two in the solid in the 2.78 to 2.99  $\mu$  region. If, as is most probable, these bands are due to OH groups, the shifts show that there must be intermolecular hydrogen bonding. The *para, para'* structures of sulfides I and II, from 2,5-dialkylphenols, follows by analogy from the structures of the dihydroxydiphenylmethanes. The structure of the latter is further supported by chemical evidence cited by Beaver and Stoffel.<sup>7</sup> Sulfide III is structurally analogous to K in the earlier paper; its structure follows unequivocally from the method of preparation. By analogy with the corresponding alkylidene compounds, it would be tempting to assign the bands at 2.99, 2.93 and 2.86  $\mu$  to intermolecularly bonded OH---O and, since it seems unlikely that there are two different OH groups, seek another explanation for the 2.84  $\mu$  bands. However, the 2.84  $\mu$  band is common to the three compounds and the work of Sears and Kitchen<sup>8</sup> shows that two methyl groups have the same hindering effect as one *t*-butyl or one *tt*-octyl group. Hence it is concluded that the 2.84, 2.83 and 2.86  $\mu$  bands are due to intermolecularly bonded OH---O. This also agrees with the assignment of the 2.86  $\mu$  band in the solid state spectra of the *p,p'*-dihydroxydiphenylmethanes.

If this conclusion is accepted then the most likely assignment of the 2.9  $\mu$  bands is to intermolecularly bonded OH---S. From Fisher-Hirschfelder models the OH---S bond in III would be ex-

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 (3) H. G. Dawson, unpublished work, private communication to Firestone Tire & Rubber Co., Nov. 9, 1950.  
 (4) L. Gattermann, *Ber.*, **32**, 1150 (1899).  
 (5) Farbwerke Meister, Lucius u. Bruening, German Patent 203,882 (1906); *Chem. Zentr.*, **79**, II, 1791 (1908).

(6) G. S. Holt and E. E. Reid, *THIS JOURNAL*, **46**, 2335 (1924).

(7a) Molarity of the OH radical.

(7) D. J. Beaver and P. J. Stoffel, *THIS JOURNAL*, **74**, 3410 (1952).

(8) W. C. Sears and L. J. Kitchen, *ibid.*, **71**, 4110 (1949).

TABLE I  
 DIHYDROXYDIPHENYL SULFIDES DERIVED FROM ALKYL CRESOLS

No.	Alkylcresol	Sulfide	M.p., °C., cor.	Sulfur, %	
				Calcd.	Found
I	2- <i>t</i> -Butyl-5-methylphenol	Di-(4-hydroxy-2-methyl-5- <i>t</i> -butylphenyl)	159.5-160	8.94	8.97, 8.79
II	2- <i>tt</i> -Octyl-5-methylphenol	Di-(4-hydroxy-2-methyl-5- <i>tt</i> -octylphenyl)	135-136	6.81	6.67, 6.61
III	2,6-Dimethylphenol	Di-(4-hydroxy-3,5-dimethylphenyl)	121.5-122	11.69	11.67, 11.91
IV	2,4-Dimethylphenol	Di-(2-hydroxy-3,5-dimethylphenyl)	93 - 93.5	11.69	11.71, 11.84
V	2- <i>t</i> -Butyl-4-methylphenol	Di-(2-hydroxy-3- <i>t</i> -butyl-5-methylphenyl)	84 - 85	8.94	8.82, 8.93
VI	2- <i>tt</i> -Octyl-4-methylphenol	Di-(2-hydroxy-3- <i>tt</i> -octyl-5-methylphenyl)	105 -106	6.81	6.69, 6.94
VII	4,6-Di- <i>t</i> -butyl-3-methylphenol	Di-(2-hydroxy-3,5-di- <i>t</i> -butyl-6-methylphenyl)	206 -207	6.81	6.83, 6.72
VIII	4,6-Di- <i>t</i> -butyl-3-methylphenol	Di-(2-hydroxy-3,5-di- <i>t</i> -butyl-6-methylphenyl) disulfide	154 -155	12.75	12.60
Reference compounds					
IX		Methyl 2-mercaptobenzoate	124 -126 <sup>a</sup>	19.06	19.52, 19.52
X		Methyl 2-methylthiobenzoate	67 - 67.5	17.59	17.48, 17.34
XI		<i>p</i> - <i>t</i> -Butylphenol (Dow, recryst.)	98.5- 99		
XII		Dibenzothiophene (Jefferson)	98 - 98.5	17.37	17.37, 17.32
XIII		2-Hydroxyphenyl methyl sulfide	75 - 80 <sup>b</sup>	22.86	22.09

<sup>a</sup> B.p. at 8 mm. <sup>b</sup> B.p. at 5 mm.

 TABLE II  
 OH BANDS IN DIHYDROXYDIPHENYL SULFIDES

No.	Sulfide	Wave lengths in microns: s means strong, m medium, w weak in band intensities; sh means shoulder.				Assignment
		Dil. CCl <sub>4</sub>	Melt	Mull		
I	Di-(4-hydroxy-2-methyl-5- <i>t</i> -butylphenyl)	2.76s sharp		2.84s sharp 2.99s broad	OH...O intermolecular OH...S intermolecular	
II	Di-(4-hydroxy-2-methyl-5- <i>tt</i> -octylphenyl)	2.76s sharp		2.83s sharp 2.93s sharp	OH...O intermolecular OH...S intermolecular	
III	Di-(4-hydroxy-3,5-dimethylphenyl)	2.75s sharp		2.78w sharp 2.86s sharp	OH...S intermolecular OH...O intermolecular	
IV	Di-(2-hydroxy-3,5-dimethylphenyl)	2.85sh 2.89s sharp	2.85sh 2.89 sharp 3.01w	2.85sh 2.90s sharp 3.01w	OH...O intramolecular OH...S intramolecular	
V	Di-(2-hydroxy-3- <i>t</i> -butyl-5-methylphenyl)	2.86w sh 2.92s sharp	2.86w sharp 2.92s sharp	2.86w sharp 2.91s sharp	OH...O intramolecular OH...S intramolecular	
VI	Di-(2-hydroxy-3- <i>tt</i> -octyl-5-methylphenyl)	2.85w sh 2.91s sharp	2.86w sh 2.93m sharp	2.85w sh 2.89s sharp	OH...O intramolecular OH...S intramolecular	
VII	Di-(2-hydroxy-3,5-di- <i>t</i> -butyl-6-methylphenyl)	2.86s sharp 2.92s sharp		2.85s sharp 2.92s sharp	OH...O intramolecular OH...S intramolecular	
VIII	Di-(2-hydroxy-3,5-di- <i>t</i> -butyl-6-methylphenyl) disulfide	2.88s sharp		2.93s sharp	OH...S intramolecular	

 TABLE III  
 OH BANDS IN SPECTRA OF SOME REFERENCE COMPOUNDS

Substance		Dil. CCl <sub>4</sub> 0.05 M	Concd. CCl <sub>4</sub> 0.5 M	Pure compound
IX	Methyl 2-mercaptobenzoate	2.92m sharp		2.84w 2.92m sharp
X	Methyl 2-methylthiobenzoate	.....		.....
XIII	2-Hydroxyphenyl methyl sulfide	2.96s sharp	2.97s sharp	2.97s sharp

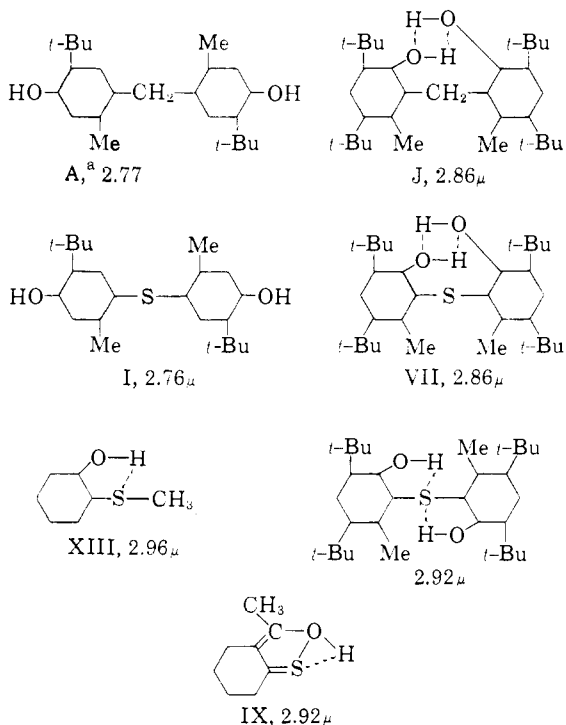
pected to be weaker than in the others on account of the adjacent methyl groups.

As Table II shows, the sulfides IV, V, VI, VII have two bands at about 2.85 and 2.9  $\mu$  in both dilute solutions and solids. Since the bands are probably due to OH, the absence of a shift in the spectra of the two states indicates that the OH groups are intramolecularly hydrogen bonded. From the method of preparation and the spectra of the corresponding *para,para'* compounds it must be concluded that these compounds are *ortho,ortho'*. Then the 2.85  $\mu$  band could be ex-

plained, by analogy with compound J of the previous paper<sup>1</sup> (see Table IV), as due to intramolecular OH---O bonding. This means that the molecules must be in the *cis* configuration, as shown for compound VII in Table IV. Since there is no band at 2.75  $\mu$  in the dilute solution spectra the 2.9  $\mu$  bands cannot be assigned to OH---O with the molecules in the *trans* configuration. Consequently the 2.9  $\mu$  bands are assigned to OH---S. It is possible, of course, that some of the molecules are in the *trans* configuration with all of the OH groups in these molecules hydrogen bonded to S.

There would be no free OH groups in this case either, and no  $2.75 \mu$  band. In such a case however, a difference in the intensities of the  $2.85$  and  $2.9 \mu$  bands could be expected, depending upon the number of molecules in the *cis* and *trans* configuration. We have no evidence regarding this.

TABLE IV  
STRUCTURES AND ABSORPTION BANDS IN DILUTE SOLUTION



<sup>a</sup> Letters refer to compounds in reference 1.

The band at  $3.01 \mu$  in the solid state or melt spectrum of compound IV, di-(2-hydroxy-3,5-dimethylphenyl) sulfide, probably is due to an OH group. Since it is not found in the spectra of similar compounds in which the methyl groups are replaced by larger groups, it probably is due to intermolecularly bonded OH, even though no evidence of free OH groups was found.

These conclusions are supported by the  $2.9 \mu$  band in the dilute solution and mull spectra of compound VIII of Table II. It is obvious that, if the band is due to OH, it cannot be due to intramolecular OH---O bonding and that intramolecular OH---S bonding is quite possible and even likely. Intermolecular OH---O bonding is eliminated since there is no  $2.75 \mu$  band in the dilute solution spectrum.

The spectrum of methyl 2-mercaptobenzoate, in this region, offers further confirmation of the existence of OH---S bonding. For this compound, as shown in Table III, there is a band at  $2.92 \mu$  in both the dilute solution and pure liquid spectra. It would be expected that this band is due to OH and this expectation is confirmed by the disappearance of the band when the hydrogen of the thiol group is replaced by a methyl group. An OH

group could be formed if the molecule existed as a tautomeric mixture of the thiol form and the quinoid form IX shown in Table IV. If so, and since there is no shift, the  $2.92 \mu$  band is due to intramolecular OH---S bonding and the weak  $2.84 \mu$  band to intermolecular OH---O bonding. These conclusions are the same as those obtained for the sulfides and disulfide above. Evidence of the existence of the quinoid form in the pure liquid of this compound probably is afforded by its yellow color.

Further evidence of OH---S bonding is given by the spectrum of 2-hydroxy-phenyl methyl sulfide, also given in Table III. There is only one band at  $2.96 \mu$  in the dilute solution and pure spectra. The band must be due to OH and the absence of a shift indicates intramolecular bonding. This is, most likely, OH---S. This may possibly explain the low OH number found for this compound,  $0.675$  OH per mole.

In view of the work of Badger and Bauer<sup>9</sup> the strength of the OH---S bond, corresponding to a shift of  $200 \text{ cm.}^{-1}$ , is somewhat surprising. However, as Bellamy<sup>10</sup> shows for OH---O bonds, the OH---S bond closes a ring in these compounds thus increasing the bond strength. Moreover, a shift of  $140 \text{ cm.}^{-1}$  for S---HS bonds has been reported<sup>11</sup> so that a shift of  $200 \text{ cm.}^{-1}$  for OH---S is not surprising. In addition, shifts of  $800 \text{ cm.}^{-1}$  for OH---Cl in hydroxylamine hydrochloride and of  $367 \text{ cm.}^{-1}$  in chloral hydrate have been reported.<sup>12</sup> In comparison a shift of  $200 \text{ cm.}^{-1}$  for OH---S does not seem unduly large.

### Conclusions

The infrared spectra of the crystalline sulfides of 2,5-dialkylphenols reported here show the 4,4'-dihydroxydiphenyl sulfide structure.

The infrared spectra of the crystalline sulfides of 2,4-dialkylphenols reported indicate that the molecules of these 2,2'-dihydroxydiphenyl sulfides exist in the *cis* configuration or partly in the *cis* and *trans* configurations.

The spectra of both types of compounds show that OH---S bonds are formed as evidenced by a band near  $2.95 \mu$ . These bonds are intermolecular in the 4,4'-dihydroxy compounds and intramolecular in the 2,2'-dihydroxy compounds.

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