

2,2'-Dihydroxybiphenyl and its Methyl Ethers: UV Absorption, Planarity and Hydrogen Bonding in Various Solvents

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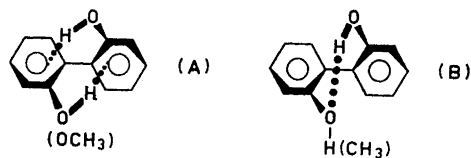
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The UV absorptions of 2,2'-dihydroxybiphenyl and its mono- and dimethyl ethers were studied in several solvents. For the two phenols, the O—H stretching frequencies were determined in heptane and/or dioxan. The UV absorptions of the two phenolic biphenyls showed an unusual dependence on the character of the solvent and on the stage of ionization. In these compounds two types of hydrogen bond may connect the two halves of the molecules. The presence or absence of those bonds depends on the nature of the solvent and, in turn, determines the conformation (with its specific degree of coplanarity) and thereby, the absorption of the solute. The additional bulk added to the 2-substituents by attached solvent molecules seems to have little influence on the planarity. The degree of planarity is highest in molecular forms containing an O—H...O bridge between the 2- and 2'-positions, lowest in the "inner π -complex" conformation. The presence of inner O—H... π bridges is indicated in 2,2'-dihydroxybiphenyl and its monomethyl ether in acidic aqueous solution.

The results reported indicate that UV absorption measurements offer an indirect means of studying the hydrogen bonding patterns of biphenyl derivatives capable of forming hydrogen bridges between the two halves of the molecules.

During attempts to characterize and determine the 2,2'-dihydroxybiphenyl elements in lignin we found that model compounds of this type (2,2'-dihydroxybiphenyl, its monomethyl ether and 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-di[hydroxymethyl]biphenyl) showed distinctly different UV absorptions in acidic water and ethanol solution. The differences observed suggested that in each compound the angle between the planes of the aromatic rings was dependent on the solvent, in other words that different conformations of the solute were prevailing in water and ethanol.

IR investigations¹⁻³ have shown that 2,2'-dihydroxybiphenyl occurs in two forms in carbon tetrachloride solution: predominantly as an "inner π -complex",² containing a hydrogen bond from each hydroxyl group to the π electron cloud of the opposite ring (conformation A), and — to about 15 % — in conformation (B), in which a hydrogen bond connects the proton of one



of the hydroxyl groups with the oxygen atom of the other, while the proton of the latter hydroxyl group does not form a hydrogen bond. The O—H stretching frequencies corresponding to the O—H $\cdots\pi$ and the O—H \cdots O groups suggest that the former type of hydrogen bond is approximately half as strong as the latter. Therefore, the (A) form with its two hydrogen bonds of the former type, and the (B) form with its one hydrogen bond of the latter type, should be approximately equally stable, as is also indicated by their co-occurrence in carbon tetrachloride solution.

The monomethyl ether of 2,2'-dihydroxybiphenyl has been found, also by IR measurements,⁴ to occur predominantly in the (B) form in carbon tetrachloride solution, and only to a smaller extent in the (A) form. The predominance of the (B) form with the monomethyl ether in contrast to the diphenol was explained⁴ by the greater tendency of the methoxyl group than of the hydroxyl group to act as a proton acceptor and by the presence of only one hydroxyl group in the monomethyl ether. (The stabilization energy gained through a single O—H $\cdots\pi$ bond cannot compete with that of the O—H \cdots O bond.) In accordance with the relatively strong tendency of the methoxyl group to act as a proton acceptor, the O—H \cdots O absorption band is located further away from that of the free O—H group (*ca.* 3605 cm⁻¹) with the monomethyl ether (3450 cm⁻¹) than with the diphenol (3500 cm⁻¹), indicating a somewhat shorter hydrogen bridge, *i.e.* a more nearly planar structure for the ether than for the diphenol in the (B) form.

UV spectrometry has been used a great deal as a means of estimating the degree of coplanarity of biphenyl derivatives.⁵ Steric or other hindrance to coplanarity in this group of substances is known to cause (1) lowering and blue-shift of the biphenyl "conjugation band" at about 250 m μ and (2) appearance of more or less distinct absorption bands at longer wavelengths. The change in strength and position of the "conjugation band" can be taken as a rough measure of the interplanar angle in the biphenyl investigated, and the position and intensity of the long-wave band(s) may give additional information in this respect. However, a detailed comparison of the interplanar angles of different biphenyl derivatives, based primarily on the absorption at about 250 m μ , is often hazardous,^{6,5} because, besides steric hindrance, auxochromic effects of different substitution may interfere with the "conjugation band". No doubt the method is safer if used for comparing the interplanar angles of different conformations of the same biphenyl, but to our knowledge comparisons of that kind have not yet been tried.

Our original observations, mentioned above, led us to study the planarity of 2,2'-dihydroxybiphenyl and its methyl ethers in various solvents by the UV method. Already in the 1920:s, Japanese workers had investigated the UV absorption of ethanol solutions of 2,2'-dihydroxybiphenyl⁷ and its dimethyl

ether,⁸ and a Polish study⁹ on the diphenol followed in 1930. Williamson and Rodebush⁶ were interested to find that the absorption curve for 2,2'-dihydroxybiphenyl in ethanol was distinctly different from that of biphenyl and "showed a maximum characteristic of phenol", even though the O—H group is a relatively small substituent, which would not be expected to cause a great steric hindrance to coplanarity. For 2,2'-dimethoxybiphenyl in hexane they found an absorption curve reminiscent of that of anisole.

Not unexpectedly, our results with the three compounds in various solvents indicated (1) that the diphenol and its monomethyl ether occurred in three conformations of different planarity in the solvents used and (2) that the

Table 1.

Compound	Solvent	UV absorption maxima Cf.			
		<i>m</i> μ	log ϵ	<i>m</i> μ	log ϵ Ref.
I. 2,2'-Dihydroxybiphenyl, m.p. 109–10°. <i>pK</i> ₁ 7.5, <i>pK</i> ₂ \geq 11.3 (pot. titr. in water **). (Musso and Matthies ⁴ found 7.56 and 11.80 [pot. titr.], 7.46 and > 13.00 [spectroscop.]. Gordon and Johnson ¹¹ found 7.56 and ca. 13.5 [spectrophotom.].)	heptane (dist. over Na)	237 *	3.73	281	3.78
	CCl ₄ ("SPECTROSOL")	—	—	282.3	3.80
	dioxan (dist. over Na)	242	3.89	284	3.86
	99 % dioxan, 0.1 N in HCl	242.3	3.91	284	3.86
	MeOH (dried with Mg, dist.), 0.06 N in HCl (dried with H ₂ SO ₄)	243	3.95	283.4	3.84
	99 % MeOH, 0.1 N in HCl	243	3.96	283.4	3.85
	95 % EtOH, 0.1 N in HCl	244.5	4.00	285	3.85
	99 % Pr ⁱ OH, 0.1 N in HCl	245	4.04	286	3.87
	99 % Bu ^t OH, 0.1 N in HCl	245	4.07	286.7	3.89
	0.01 N HCl	237.8	3.79	279	3.76
	pH 9.5 glycine buffer soln.	248	3.95	308.9	3.93
	2 N NaOH			301.2	3.86
	5 N NaOH			301	3.87
	90 % EtOH, N in KOH	250	3.95	311.2	3.91
	II. 2-Hydroxy-2'-methoxybiphenyl, prepd. ¹² from 2,2'-dihydroxybiphenyl with CH ₂ N ₂ in dry ether. Recryst. from EtOH and AcOH, m.p. 71.5–73°. <i>pK</i> 9.9 (pot. titr. in water). (Ref. ⁴ : m.p. 73–4°, <i>pK</i> 10.4 [spectroscop.].)	heptane (dist. over Na)	245	3.97	282
CCl ₄ ("SPECTROSOL")		—	—	284	3.85
99 % dioxan, 0.1 in HCl		240	3.86	282	3.85
99 % MeOH, 0.1 N in HCl		238.9	3.84	281	3.81
95 % EtOH, 0.01 N in HCl		239	3.84	282	3.80
99 % Pr ⁱ OH, 0.15 N in HCl		239	3.86	282	3.81
99 % Bu ^t OH, 0.1 N in HCl		240	3.87	282.3	3.80
0.01 N HCl		239	3.77	278	3.74
N NaOH				281	3.56
95 % EtOH, 0.1 N in KOH				299	3.71
			282	3.49	
			304.5	3.71	
III. 2,2'-Dimethoxybiphenyl, ¹³ m.p. 156–6.5°.	heptane (dist. over Na)	238	3.88	280	3.83
	dioxan (dist. over Na)	240	3.84	281	3.83
	99 % dioxan, 0.1 N in HCl	240	3.83	281	3.82
	dioxan/water (1:1 by vol.)	240	3.81	280	3.80
	95 % EtOH	239	3.84	280	3.80
	99 % Bu ^t OH, 0.1 N in HCl	239	3.87	281	3.82

* Numbers printed in Italics denote points of inflexion.

** The values given in Ref.¹⁰ are erroneous.

hydrogen bonding properties of the solute and the solvent were the factors determining the conformation of the solute or the solute-solvent complex in each solution. Therefore, the hydrogen bonding was studied separately for some of the solutions by means of IR determinations of the O—H stretching frequencies.

EXPERIMENTAL

Table 1 gives brief data on the preparation and properties of the compounds investigated. It also lists the solvents used for the UV measurements. A little hydrochloric acid was added to several solvents as a safety precaution against unwanted ionization (the diphenol is partly ionized at least in water, methanol and ethanol) and — with *t*-butanol solutions — to prevent crystallization. In general no effort was made to keep the alcohols and the dioxan free from water for the UV measurements, since in the cases tried (I in acidic methanol, I and III in dioxan, Table 1) no significant change of absorption was found on drying the solvents. Besides, each solution of I or II in a moist organic solvent showed an absorption so different from that of the aqueous solution that one must conclude that the water present in the organic solvent had little or no influence on the absorption curve.

The alkaline aqueous solvents were chosen so as to give as nearly pure solutions as possible of the ions of the solutes. However, a complete ionization of the 2,2'-dihydroxybiphenyl was not achieved. The normal ethanolic potassium hydroxide solution caused even less ionization of the diphenol than the strong aqueous alkali.

A Zeiss PMQ II spectrophotometer with calibrated 1 cm silica cells was used for the UV absorption measurements. Readings were taken at intervals not exceeding 5 $m\mu$ or, when desirable, 1–2 $m\mu$, and $\log I_0/I$ readings were kept between 0.1 and 1.5 by using suitable dilution. The maxima and points of inflexion observed in the extinction curves are listed in Table 1. Several of the absorption curves are reproduced in Figs. 1–5.

The IR absorption in the O—H stretching region was determined for the diphenol in heptane and dioxan and for its monomethyl ether in dioxan only, since its solubility in heptane is very low. A Perkin-Elmer 21 instrument and 1 mm cells were used. The results are given in Table 2.

RESULTS AND DISCUSSION

For 2,2'-dihydroxybiphenyl in heptane only one IR band was found in the O—H stretching region, namely a narrow band at 3550 cm^{-1} (Table 2). The shape and position of this band suggest that it is of the same origin as the 3560 cm^{-1} band^{1,3} of 2,2'-dihydroxybiphenyl in carbon tetrachloride. Even the UV absorption curves of the compound in the two solvents (in the wavelength region available with carbon tetrachloride) (Fig. 1) are very similar. The only reasonable conclusion seems to be that the "inner π -complex" conformation (A) is the predominating form in heptane, just as in carbon tetrachloride.

Table 2.

Compound	Solvent	O—H str. band, cm^{-1} , width
2,2'-Dihydroxybiphenyl	heptane (dist. over Na)	3550 (narrow)
	dioxan (dist. over Na)	ca. 3320 (wide)
2-Hydroxy-2'-methoxybiphenyl	dioxan (dist. over Na)	ca. 3340 (wide)

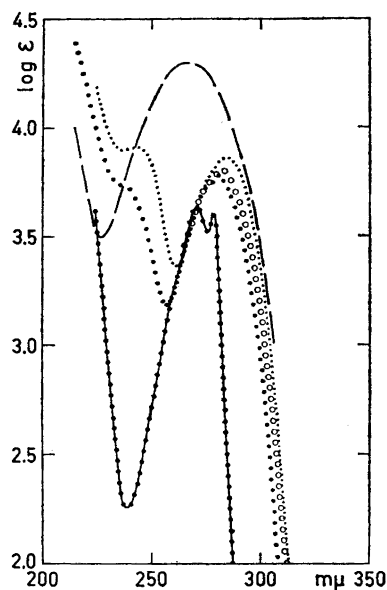
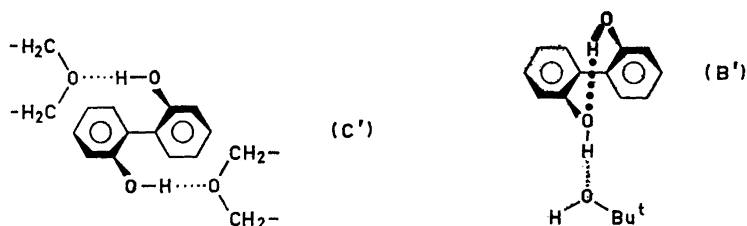


Fig. 1. Absorption curves for 2,2'-dihydroxybiphenyl in heptane (● ● ● ●), carbon tetrachloride (○ ○ ○ ○) and acidic 99 % dioxan (.....), for two moles of *o*-cresol in heptane¹⁴ (●—●—●) and for 4,4'-dihydroxybiphenyl in ethanol⁶ (— —).

As seen from Fig. 1, the UV absorption of this form is characterized by a low "conjugation band", visible as a "shoulder" slightly below 240 $m\mu$, and by a long-wave absorption band less than twice as intense and at only about 10 $m\mu$ longer wavelength than the maximum of two molecules of *o*-cresol in heptane.¹⁴ In contrast, 4,4'-dihydroxybiphenyl,⁶ in which there is considerably less steric hindrance to coplanarity, shows only one absorption band, an intense "conjugation band". It is evident that the conjugation between the two aromatic rings in the "inner π -complex" form of 2,2'-dihydroxybiphenyl is low, in other words that the angle between the ring planes is large. As we shall see later, it is larger than in form (B), for which molecular models suggest an angle of at least about 30°. On the other hand, the presence of a "conjugation band" and the position and intensity of the long-wave band point to a certain degree of interaction between the two halves of the (A) molecule. Unless this is a case of chromophoric interaction without conjugation (Longuet-Higgins and Murrell¹⁵), the interplanar angle in the (A) type molecule is appreciably smaller than 90°.

In dioxan 2,2'-dihydroxybiphenyl exhibits only one IR band in the O—H stretching region, a wide band whose position (*ca.* 3320 cm^{-1} , Table 2) suggests hydrogen bonding of a much stronger type than those found in carbon tetrachloride and heptane solutions. Dioxan being a potent hydrogen acceptor, we conclude that both of the phenolic protons are bound to dioxan molecules and that the intramolecular hydrogen bonds are lost (form C'). The two UV absorption bands of the diphenol in dry dioxan or acidic moist dioxan are considerably more intense and occur at longer wavelengths than those of the heptane and carbon tetrachloride solutions (Table 1, Fig. 1). This suggests



that in the "open" complex (C') the two phenyl rings are more nearly conjugated, *i.e.* less twisted from coplanarity than in form (A).

Fig. 2 shows the extinction curves of 2,2'-dihydroxybiphenyl in some acidified alcohols, primary, secondary and tertiary. The methanolic solution shows roughly the same absorption curve as the dioxan solution (Fig. 1). Higher wavelength and intensity values of both absorption maxima are found as the alcohols become longer and more branched, until for the *t*-butanol solution we observe the highest values found with any of the acidic solvents. This indicates that at least two solute forms are present side by side in the alcoholic solutions, the more planar form being especially abundant in *t*-butanol solution. Since the conformations (A) and (C) could be assigned to the structures predominating in heptane and dioxan, respectively, it is probable that the third form, (B), linked to the alcohol via the "free" phenolic proton as in (B'), is the "new" form giving the *t*-butanol solution its high absorption. Molecular models indicate that (B) may well be the most nearly planar of the three conformations, with an interplanar angle perhaps not larger than about 30°. The stability in *t*-butanol solution of form (B) rather than (C), the form stable in dioxan, seems to be due to the fact that the butanol is a weaker proton acceptor than dioxan and, therefore, cannot break the intramolecular hydrogen bond of the diphenol in the (B') form, particularly since that bond is no doubt strengthened by the intermolecular one. Molecular models indicate that the *t*-butanol molecule bound to one of the phenolic protons does not exert any considerable steric hindrance to the approach of a second *t*-butanol molecule to the second phenolic proton.

Due to the inductive effect of the alkyl groups, *t*-butanol would be expected to have the highest tendency of the alcohols to act as a proton acceptor towards the phenol, the other alcohols following in the order of decreasing alkyl groups. The lower average planarity of 2,2'-dihydroxybiphenyl in ethanol and methanol than in isopropanol and *t*-butanol may, therefore, perhaps be explained by the lower alcohols acting to a larger extent than the higher ones as proton donors rather than proton acceptors towards the phenol, giving rise to complexes of the type occurring in water (see below).

In acidic aqueous solution (Fig. 2) the compound exhibits nearly the same absorption as in heptane and carbon tetrachloride (Fig. 1), the difference in the long-wave band, if significant to planarity, indicating an even lower average degree of coplanarity in the aqueous solution. This immediately suggests that the "inner π -complex" form, which is present to about 85 % in carbon tetrachloride, is also present and perhaps even more dominating in

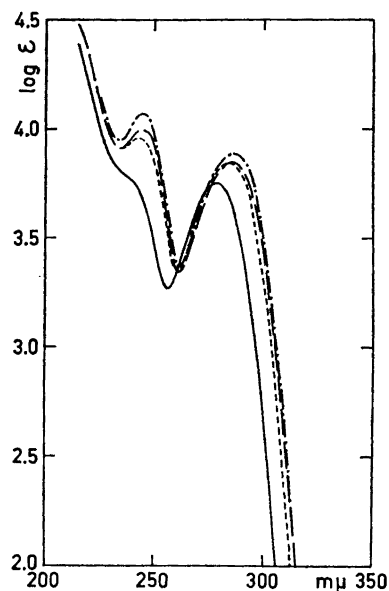
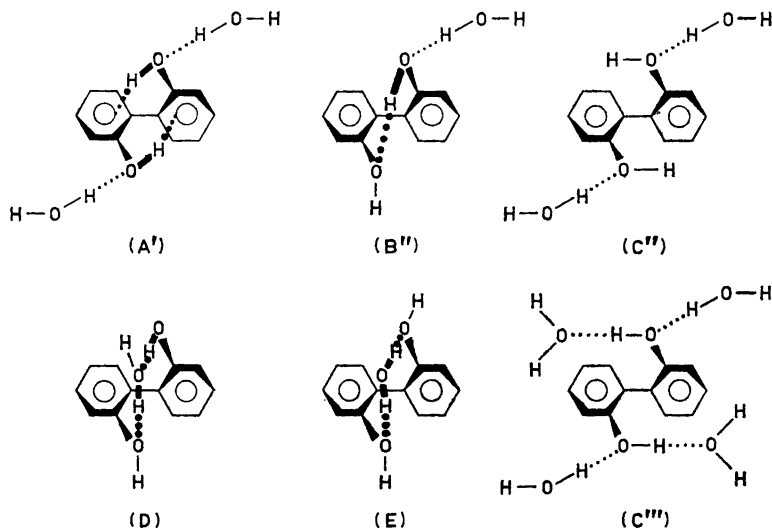


Fig. 2. Absorption curves for 2,2'-dihydroxybiphenyl in acidic 99 % methanol (---), acidic 95 % ethanol (—), acidic 99 % *t*-butanol (— · — · —) and 0.01 N hydrochloric acid (— — —).

aqueous solution. Water being a somewhat stronger acid than the diphenol, it seems reasonable to assume that hydrogen bridges are formed between water as, predominantly, a proton donor and the phenol as an acceptor. Various complexes of this type are conceivable, the intramolecular hydrogen bonds of the diphenol being either retained, as for instance in (A') and (B''), or broken, as in (C''), (D), (E) or (C'''). The low degree of planarity indicated by the



UV absorption makes forms like (B''), involving an inner O—H...O bridge unlikely. The "open" form (C''), in order to account for the UV absorption, would have to possess an interplanar angle very similar to that of form (A). In such a case, however, it must be expected either to "close up" to form (A') or possibly to be stabilized, *e.g.* as in (C'''), by two more water molecules acting as acceptors towards the "free" phenolic protons. However, it does not seem probable that (C''') would have an interplanar angle sufficiently different from that of the phenol-dioxan complex (C') to account for the UV absorption of the aqueous solution. Molecular models indicate that complexes like (D) and (E) might have large enough interplanar angles. However, if a complex of type (D) is stable in water, one would expect a similar type of complex to predominate in the acohols, the O—H group of the alcohol forming the bridge between the phenolic hydroxyl groups. Type (E) complexes, on the other hand, might be expected to form at least as easily in the dioxan/water (1:1) solution of the dimethyl ether as in the aqueous solution of the diphenol. Yet the UV absorption of the latter solution does not indicate that the dimethyl ether forms such complexes with the water molecules.

Arguments of this kind have led us to the hypothesis that either (A') with additional water molecules attached to the ones that are directly bound to the solute, or possibly a complex of, *e.g.*, type (D) or (E), also further hydrated, is the form predominating in acidic aqueous solutions of 2,2'-dihydroxybiphenyl. As will be seen below, the hypothesis that form (A') predominates leads to no contradictions in the discussion of the absorption of the methyl ethers in various solvents.

As was mentioned in the introduction, IR investigations have shown that 2-hydroxy-2'-methoxybiphenyl occurs mainly in conformation (B) in carbon

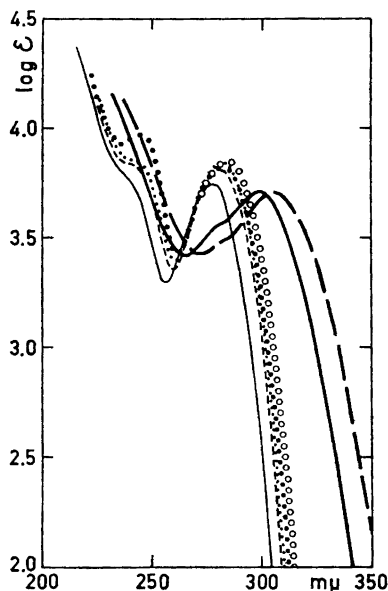


Fig. 3. Absorption curves for 2-hydroxy-2'-methoxybiphenyl in heptane (●●●●), carbon tetrachloride (○○○○), acidic 99% methanol (-----), acidic 99% dioxan (.....), 0.01 N hydrochloric acid (————), 1 N sodium hydroxide solution (————) and 0.1 N ethanolic potassium hydroxide solution (———).

tetrachloride solution. As the parent diphenol occurs mainly in form (A) in this solvent, it is not surprising that the two solutions differ considerably as regards their UV absorption (Figs. 3 and 1) and that the difference indicates that the monomethyl ether has the higher average planarity of the two solutes.

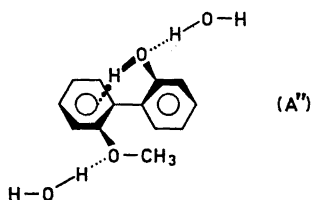
Just as with the diphenol, a change from carbon tetrachloride to heptane causes only a slight violet-shift and reduction of the intensity of the long-wave UV absorption band of the monomethyl ether (Fig. 3), suggesting that the relative abundances of forms (A) and (B) are roughly the same in both solvents. The proportion of conformation (B) seems to be lower in these solutions than in the acidic *t*-butanol solution of the parent diphenol, whose UV absorption (Fig. 2) indicates a higher average degree of conjugation.

The UV absorption curves of the acidic methanol and ethanol solutions of the diphenol (Fig. 2) are rather similar to that of the monomethyl ether in heptane (Fig. 3). This may perhaps be taken as a support for the suggestion above that those diphenol solutions contain conformations (A) and (B) side by side.

In dioxan the monomethyl ether exhibits one IR band only in the O—H stretching region, a wide maximum at *ca.* 3340 cm^{-1} (Table 2), indicating that all of the solute molecules are strongly hydrogen bonded to the dioxan via the phenolic proton. A comparison of the UV extinction curve for the monomethyl ether in acidic 99 % dioxan (Fig. 3) with that of the diphenol in the same solvent (Fig. 1) shows that there is a small difference between the two. If this difference is relevant to planarity, it suggests a somewhat higher planarity for the diphenol, indicating that an *o*-methoxyl group constitutes a slightly greater steric hindrance to coplanarity than an *o*-hydroxyl group with attached dioxan.

The acidic alcohol solutions of the monomethyl ether (Table 1 and Fig. 3) all show nearly the same absorption curves, closely approaching that of the dioxan solution. Evidently, hydrogen bonds between the phenolic proton and the solvent are formed to a great extent even in the alcohols, yet slightly less in methanol and ethanol than in the higher alcohols. Just as with the diphenol, the primary alcohols again seem to act partly as proton donors, allowing the existence of inner O—H $\cdots\pi$ bonds (*cf.* (A''), below) in some of the solute molecules.

In acidic water solution the monomethyl ether (Fig. 3) exhibits practically the same UV absorption as the parent diphenol (Fig. 2). A comparison with the other curves in Fig. 3 shows that the aqueous solution contains the least planar form of the solute. Just as with the diphenol, the "inner π -complex" form (A'') or possibly an "open" form of type (D) or (E), heavily associated with water, seems to be predominating in the acidic aqueous solution. A type



(B) conformation would be too nearly planar to account for the UV absorption. Besides, it is unlikely to be stable, because the hydrogen bridge that probably exists between a water molecule and the oxygen atom of the methoxy group must be expected to decrease the tendency for this oxygen atom to take part also in an internal O—H...O bond.

2,2'-Dimethoxybiphenyl is not soluble enough in water to allow a determination of its UV absorption in this solvent. Solutions in several other solvents and solvent mixtures were investigated (Table 1). In all cases mutually similar absorption curves were found (Fig. 4), with points of inflexion at about 240 m μ . (Cf. Williamson and Rodebush,⁶ who found no "conjugation band".) It is evident that the interplanar angle of the solute — which, lacking OH groups, can only exist in the "open" form (C) — is largely unaffected by solute-solvent hydrogen bonds, which must be assumed to be absent in at least heptane and dry dioxan but present in at least the alcohols.

It was mentioned above, that the parent diphenol seems to be slightly more planar in acidic 99 % dioxan than the monomethyl ether in the same solvent. Less planar still, according to the UV absorption, is the dimethyl ether in dioxan (Fig. 4). In other words, an *o*-methoxyl group again seems to be more "bulky" than an *o*-hydroxyl group with dioxan attached to it.

The geometrical forms so far discussed, then, can be listed in order of decreasing planarity as shown in Table 3.

The acidities of 2,2'-dihydroxybiphenyl and its monomethyl ether were recently determined and discussed by Musso and Matthies⁴ and that of 2,2'-dihydroxybiphenyl by Gordon and Johnson.¹¹ The p*K* values found by those authors as well as the values determined independently by us are given in Table 1. Our value for the monomethyl ether, obtained by potentiometric

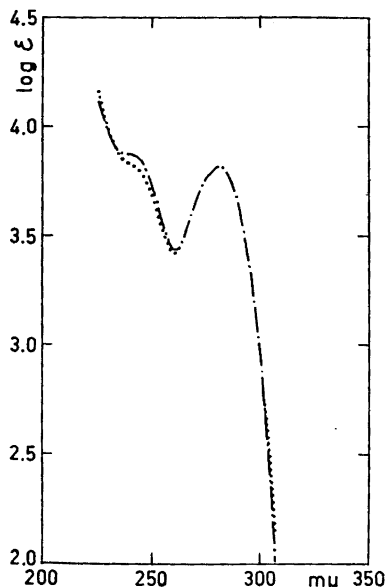
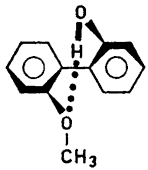
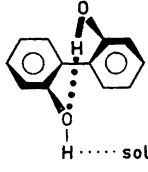
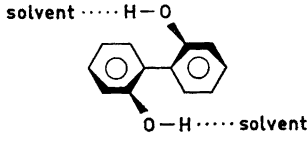
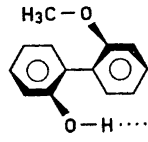
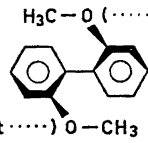
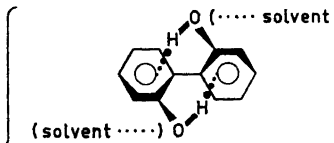
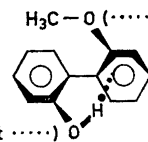


Fig. 4. Absorption curves for 2,2'-dimethoxybiphenyl in acidic 99 % dioxan (.....), and acidic 99 % *t*-butanol (— · — · —).

Table 3. Geometrical forms, in order of decreasing planarity.

Type of conformation	Species	Well represented in
B		carbon tetrachloride, heptane
B		acidic <i>t</i> -butanol
C		dioxan
C		dioxan
C		most solvents
A		water(?), heptane, carbon tetrachloride
		

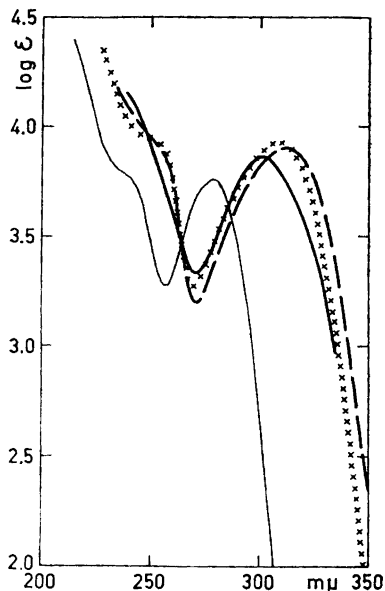


Fig. 5. Absorption curves for 2,2'-dihydroxybiphenyl in 0.01 N hydrochloric acid (—), pH 9.5 glycine buffer solution (x x x), 5 N sodium hydroxide solution (—) and 1 N, 90% ethanolic potassium hydroxide solution (---).

titration, is 0.5 units lower than the one found by the German authors, using a spectrophotometric method. For the diphenol itself, the three investigations gave similar values, at least for the first ionization constant.

As is seen from Fig. 5, the ionization of one of the hydroxyl groups in 2,2'-dihydroxybiphenyl (the glycine buffer solution) causes a very strong red-shift of the UV absorption curve of this compound. This suggests a more deep seated change on ionization than mere loss of a proton, namely the change to a more nearly planar conformation. The mono-ion is characterized by a strong inner O—H...O⁻ bridge,^{4,11} and it was shown above that O—H...O bridges between the 2- and 2'-positions give this type of molecule a relatively high degree of planarity, higher the stronger the bridges are. Therefore, it is not surprising that the mono-ion absorbs almost like a fully conjugated system, with one single long-wave band, albeit widened towards shorter wave-lengths, because each half of the molecule still acts to some extent as a separate chromophore.

The pK_2 value for 2,2'-dihydroxybiphenyl is very high, probably over 13. Even a comparison of the UV absorption curves of the compound at pH 9.5, in 2 N and in 5 N sodium hydroxide solution (Table 1, Fig. 5) indicates that ionization in the latter solvent is not complete (approximately 80–90% di-ion). When the di-ion is formed, the inner O—H...O⁻ bridge is lost and the planarity decreases considerably, as is seen from the loss of the pronounced "conjugation band" as well as from the violet-shift and intensity decrease of the long-wave absorption band. The di-ion evidently does not assume a coplanar form with the two substituents in the *trans*-position. The repulsion between the two ionic centres evidently is not strong enough to overcome the steric hindrance exerted by themselves and the hydrogen atoms in the other *o*-positions.

The UV absorption curve for 2,2'-dihydroxybiphenyl in normal 90 % ethanolic potassium hydroxide solution (Fig. 5) shows a shoulder at about 250 $m\mu$ and an unsymmetrical long-wave band. Those features indicate a higher average coplanarity than in the 5-normal aqueous sodium hydroxide solution, certainly due to a lower degree of ionization. In fact, the curve for the ethanolic potassium hydroxide solution is so similar to that of the glycine buffer solution, that the solution seems to contain mainly the mono-ion of the diphenol.

The anion of the monomethyl ether has a much lower planarity than the mono-ion of the diphenol, as shown by several features of the UV absorption both in aqueous and ethanolic solution (Fig. 3): the absence of an inflexion at about 250 $m\mu$, the presence of one at 281–2 $m\mu$ and the low wavelength and intensity values of the long-wave maximum. The low degree of planarity is expected, the ion of the ether having no opportunity to form an inner O—H...O bridge.

The different chromophoric characters of the diphenol di-ion and the monomethyl ether ion make it useless to attempt a comparison of their degree of planarity. It can only be stated that they are both much more twisted from coplanarity than the diphenol mono-ion, which is the most nearly planar of all solute forms investigated in this paper.

Acknowledgements. The authors thank Statens Tekniska Forskningsråd and Cellulosaindustriens Forskningsstiftelse, 1959 års fond for financial assistance, docent Sture Forsén for valuable discussions, Miss Gurli Hammarberg for determining the IR curves and Dr. James McKay for correcting the manuscript.

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Received May 8, 1963.