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HYDROGEN BONDING IN PHENOLS—V[1]

ALKYL SUBSTITUTED BIS-(HYDROXYPHENYL) ALKANES AND SIMILAR COMPOUNDS

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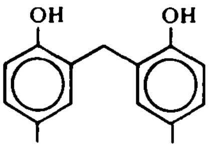
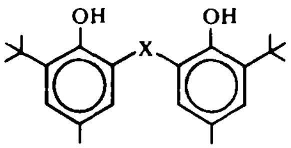
Abstract—Conformational analyses of eleven alkyl substituted bis-(hydroxyphenyl) alkanes, sulphides, disulphides and selenides have been carried out by IR, UV and NMR spectroscopy and by osmometry. Measurements reveal that these compounds exist in well-defined conformations in which the OH$\cdots\pi$ and OH$\cdots$O$\cdots$bonds are observed. Their conformational stability has been examined in pyridine.

CONFORMATIONAL analysis of some polyphenolic compounds of the novolac type has already been the subject of IR studies.[1–7] It is well-known that dinuclear novolacs [bis-(hydroxyphenyl) alkanes] fully substituted on the central aliphatic carbon can adopt well-defined complexes explained by the presence of the OH$\cdots\pi$ and OH$\cdots$O bonds.

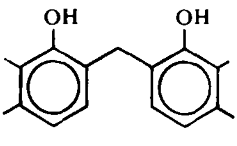
In this work we have encountered several types of bis-(hydroxyphenyl) compounds where intramolecular interaction, presumably, of the OH$\cdots\pi$ type, is present. Six types of bis-(hydroxyphenyl) compounds have been examined:



I

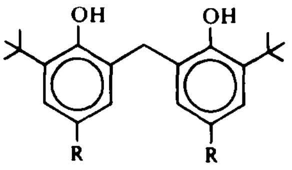


II



III

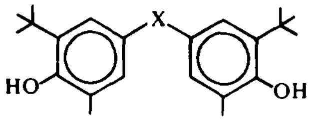
IIa X = —CH_2—
IIb X = —S—
IIc X = —S—S—
IId X = —Se—



IV

IVa $R = -C_2H_5$

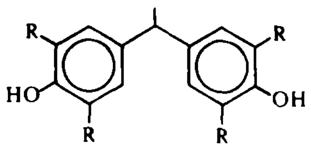
IVb $R = -C(CH_3)_3$



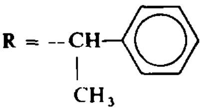
V

Va $X = -CH_2-$

Vb $X = -S-$



VI



$R = -CH(CH_3)-C_6H_5$

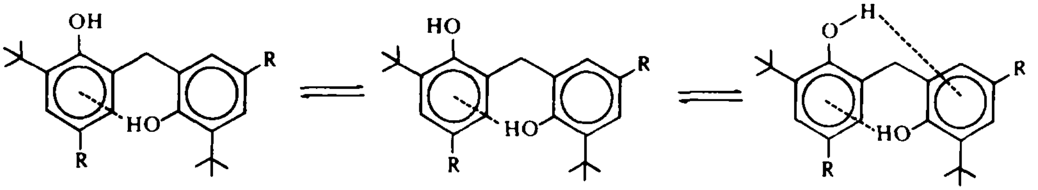
Here we report very strong intramolecular OH···π bonding in compounds II, III and IV and compare our results with those reported in the literature.[3,6] The data obtained by studying the compounds investigated are interpreted in terms of conformational equilibria.

RESULTS AND DISCUSSION

Previously we examined the IR of three polyphenols of novolak type. It was reported that in CCl_4, these flexible molecules, in which the aromatic nuclei are linked by methylene bridges, assume well-defined conformations involving the OH···OH type of intramolecular and intermolecular hydrogen bonds. In this work are compared eleven alkyl substituted bis-(hydroxyphenyl) compounds. Compound I is representative of the type of dinuclear novolac discussed in Part III[4] where it was found that in the absence of *ortho*-substituents the OH···OH intra-bonding is dominant at low concentrations (5 → 0·5 mM), but is superseded by dimerisation (involving a complete ring of four hydrogen bonded OH's) at higher concentrations (5 → 100 mM). The *ortho*-disubstituted bis-(alkylphenyl) compounds (IIa, IIb, IIc, IId, IVa, IVb, Va, Vb and VI) exemplify the type of heavily hindered phenols for which intermolecular association is difficult and which permit an assessment of the competing intramolecular hydrogen bonding. The bulky *ortho*-alkyl substituents prevent intermolecular association at all concentration levels as fully confirmed by mol wt estimation in CCl_4 (vapour pressure method).

As can be seen from the IR spectra (Table 1 and 2) the free OH's are observed only in compounds I, IIa, III, IVa, IVb, Va, Vb and VI. The bands, assigned to the stretching vibrations of the O—H group (compounds I, III, Va, Vb and VI) (Table 1 and 2) are concentration dependent. Data on compounds I and III indicate dimeric association (OH···OH type) whilst those on compounds Va and Vb reveal no association. The broad, concentration dependent band at 3225 cm^{-1} ($\Delta\nu_{\frac{1}{2}}$ 330 cm^{-1}, ε_a, 190 l $mole^{-1}$ cm^{-1}; compound III; Table 2) we assign to the closed ring of hydrogen bonds.

Compounds IIa, IVa and IVb (Table 1 and 2) have more complex spectra, though introduction of the *ortho*-di-t-butyl groups prevents self-association. All these compounds display four concentration independent bands in the OH region in CCl_4; compound IIa, 3648 cm^{-1}, 3623 cm^{-1}, 3516 cm^{-1} and 3444 cm^{-1}; compound IVa, 3648 cm^{-1}, 3632 cm^{-1}, 3516 cm^{-1} and 3450 cm^{-1}; compound IVb, 3647 cm^{-1}, 3628 cm^{-1}, 3516 cm^{-1} and 3450 cm^{-1} (Table 1). The first bands are characteristic of a hindered free OH group where the OH group is directed towards a t-butyl group. With these compounds several conformers may be in equilibrium. Thus, for CCl_4, we suggest mainly three conformers are present in compounds IIa, IVa and IVb (Table 1).



A
ν(OH) free 3620 cm^{-1}
ν(OH) bonded 3516 cm^{-1}

B
ν(OH) free 3647 cm^{-1}
ν(OH) bonded 3516 cm^{-1}

C
ν(OH) bonded 3450 cm^{-1}

According to ε_a of the band at 3620 cm^{-1} (Table 1) assigned to the free OH, it can be assumed that the conformation A is more favourable than that of B. The bands at 3450 cm^{-1} are assigned to the intramolecular OH···benzene ring (the OH···π type of hydrogen bonds). Support for this assignment is adduced from the presence of only one absorption band, ν(OH···π), 3439 cm^{-1}, in the spectrum of compound IIc (Table 1 and 2).

The conformers A and C involving the intramolecular OH···π type of hydrogen bond (according to ε_a) are more favoured in CCl_4 than those in $CHCl_3$ as can be seen by the increased intensity of the bands at 3450 cm^{-1} and 3516 cm^{-1} at the expense of the absorption bands at 3620 cm^{-1} and 3516 cm^{-1} (Table 1 and 2). The relatively constant wavenumber of the bands at ~3516 cm^{-1} and 3450 cm^{-1} in CCl_4 and $CHCl_3$ suggests that the π-bonded OH groups in these conformations are relatively inaccessible to solvent molecules, which would indicate that non-polar solvents favour conformations in which alkyl groups are directed towards the solvent molecules and the OH's are directed into the interior of the molecule.

It is very interesting that compounds IIb and IId (Table 1 and 2) exhibit only two absorption bands in CCl_4 and $CHCl_3$, which are assigned to the two different intramolecular OH···π hydrogen bonds. The simplest explanation seems to be that equilibrium involves two conformers *viz.* Dreiding molecular models of compound IIb (Figure 1).

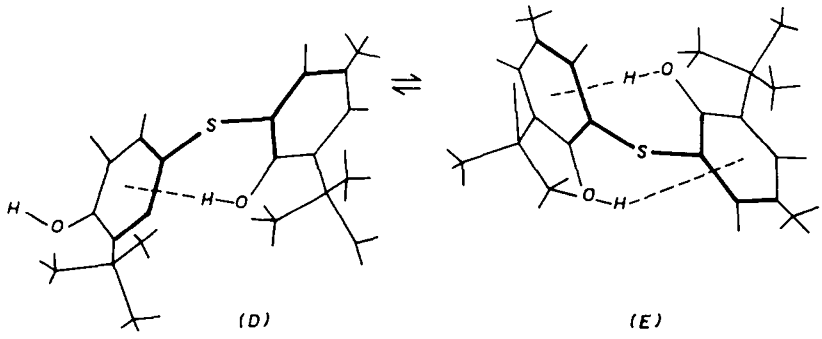
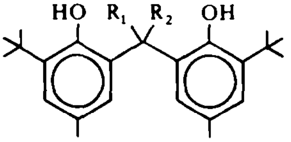


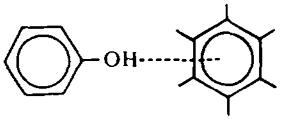
Fig 1. Planar projection of Dreiding models of the two conformers adopted by compound IIb. The dotted lines indicate the H-bonds.

In conformer E one OH group is bonded to π-electrons of the benzene ring and simultaneously to the other OH group. This possibility of hydrogen bonding has already been suggested by Coggeshall.[6] However, in this case the OH bonds must be twisted out of the plane of the benzene rings. Support for this assignment was adduced from the infrared data of bis-(hydroxyphenyl) compound VII,[3] fully substituted on the central aliphatic carbon in the spectrum of which only one band at 3484 cm^{-1} in CCl_4 is observed, and from the data of the charge-transfer complex of phenol VIII with hexamethylbenzene [ν(OH) bonded, 3506 cm^{-1}]; the bonding shift, $\Delta\nu = 100$ cm^{-1} [8,9] and from the data of substituted phenols with alkylated benzenes.[10]



VII

ν(OH) bonded 3484 cm^{-1}



VIII

ν(OH) bonded 3506 cm^{-1}

Compound IIc (Table 1 and 2) however, showed only sharp intense band in CCl_4 at 3439 cm^{-1}, $\Delta\nu_{\frac{1}{2}}$, 39 cm^{-1}, ε_a, 230 l $mole^{-1}$ cm^{-1} (in $CHCl_3$ at 3440 cm^{-1}, $\Delta\nu_{\frac{1}{2}}$, 50 cm^{-1}, ε_a, 190 l $mole^{-1}$ cm^{-1}), demonstrating that the intramolecularly hydrogen bonded conformation is undisturbed in these solvents. The single narrow absorption band indicates that both OH's must be similarly bonded intramolecularly to the adjacent benzene rings. The narrowness of this absorption band observed in both solvents implies a rigid well-defined complex. Examination of a Dreiding model of

Table 1. Hydroxyl stretching absorptions of bis—phenols in CCl_4

Compound No.	Conc. (mM)	Cell paths (mm)	ν(OH)								
			Free			Bonded					
			ν	$\Delta\nu_{\frac{1}{2}a}$	ε_a	ν	$\Delta\nu_{\frac{1}{2}a}$	ε_a	ν	$\Delta\nu_{\frac{1}{2}a}$	ε_a
I	50	0·5	3609	--	65	3463	--	--	3292	270	180
IIa[b]	50	0·5	3o23	29	105	3444	—	110	3506	75	220
IIb	50	0·5				3419	70	150	3500	..	75
IIc	100	0·1				3439	39	230	—	—	—
IId	100	0·1				3416	70	125	3488	-	80
IV[a]	100	0·2	3639	35	125	3516	70	235	3450	—	125
IVb[a]	100	0·2	3639	35	120	3516	95	205	3450	-	125
Va[b]	100	0·2	3618	20	245						
Vb[c]	100	0·2	3618	20	290						
VI	100	0·1	3648	18	740						

ν and $\Delta\nu_{\frac{1}{2}a}$ are in cm^{-1}; ε_a are in l $mole^{-1}$ cm^{-1}.

[a] shoulder at ~3620 cm^{-1}.

[b] additional bands at 3648 cm^{-1} (ε_a, ~ 60 l $mole^{-1}$ cm^{-1})

[c] additional band at 3647 cm^{-1}, (ε_a, 85 l $mole^{-1}$ cm^{-1}); —not measured.

TABLE 2. HYDROXYL STRETCHING ABSORPTIONS OF BIS—PHENOLS IN $CHCl_3$

Compound		Free		ν(OH)		Bonded			
No.	ν	$\Delta\nu_{\frac{1}{2}a}$	ε_a	ν	$\Delta\nu_{\frac{1}{2}a}$	ε_a	ν	$\Delta\nu_{\frac{1}{2}a}$	ε_a
IIa	3616	32	110	3516	185	100	3432	185	110
IIb				3490	—	60	3420	81	130
IIc							3440	50	190
IId				3480	110	65	3418	110	120
III	3593	—	45				3225	330	190
IVa	3622	40	155	3515	110	140	3437	110	140
IVb	3623	40	160	3515	105	120	3438	105	130
Va	3610	27	230						
Vb	3608	30	205						
VI	3645	23	595						

For symbols see Table 1.

Concentration 100 mM; cell paths in compounds IIa–IId and VI, 0·1 mm and in other compounds 0·2 mm, respectively.

A wavenumber shift from 3616 → 3621 over a range of concentration 100 → 10 mM was observed; — not measured.

compound IIc (Figure 2) shows that the interacting groups are within bonding distance, that is the O· · ·O distance ~3 Å.

Compounds Va and Vb (Table 1) show two OH absorptions in CCl_4, resulting from the presence of two conformations in which the conformation with the OH group (according to ε_a of the band at lower wavenumbers) directed towards the Me group is dominant. In these compounds the OH· · ·π hydrogen bonding is evidently eliminated.

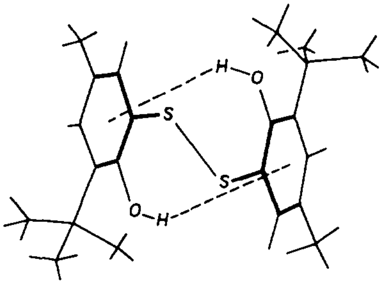
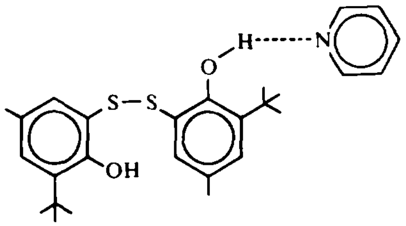


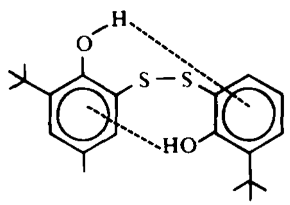
FIG 2. Planar projection of Dreiding model of compound IIc. The dotted lines indicate the H-bonds.

Compound VI, the most heavily substituted phenol of the compounds investigated displays a single sharp ν(OH) absorption at 3648 cm^{-1}, $\Delta\nu_{\frac{1}{2}}$, 18 cm^{-1}, ε_a, 740 l $mole^{-1}$ cm^{-1} in CCl_4 and at 3646 cm^{-1}, $\Delta\nu_{\frac{1}{2}}$, 23 cm^{-1}, ε_a, 595 l $mole^{-1}$ cm^{-1} in $CHCl_3$ indicating that the stretching vibrations of the O—H bond are almost unaffected by solvents, which can be explained by the fact that the OH group is sterically protected from the solvent molecules.

To test the stability of the conformations adopted by the compounds studied, eight compounds have been investigated in pyridine. Compounds IIa, IIb and IIc display two very broad absorption bands (Table 3) in which the lower wavenumber band is assigned to the OH···N hydrogen bond, i.e. the OH···π conformation is broken whilst the higher wavenumber band is assigned to the OH···π intramolecularly bonded hydroxyls, for instance, compound IIc



ν(OH) bonded, 3185 cm^{-1}



ν(OH) bonded, 3430 cm^{-1}

Table 3. Hydroxyl stretching absorptions of bis— phenols in nujol and pyridine

Compound No.	Nujol ν	$\Delta\nu_{\frac{1}{2}a}$	ν	$\Delta\nu_{\frac{1}{2}a}$	Pyridine ν	$\Delta\nu_{\frac{1}{2}a}$	ε_a	ν	$\Delta\nu_{\frac{1}{2}a}$	ε_a
I			3165							
IIa	3608	13	3394	30						
IIb	3487	—	3420	—	3370	—	80	3180	300	120
IIc	3455	sh	3438	30	3430	—	80	3185	300	115
IId	3482	—	3402	20	3370	—	—	3180	—	—
III			3180	260				3180	315	210
IVa	3530	25						3185	—	175
IVb	3532	20								

For symbols see Table 1.

Concentration in pyridine 200 mM; cell paths 0·1; concentration 5 mg/15 mg nujol; — not measured.

Table 4. UV absorption spectral data for bis—phenols (in cyclohexane)

Compound No.	Conc. (mM)	λ_{max} (nm)	log ε	λ_{max} (nm)	log ε
IIa	2·5	287	4·73	281	4·73
IIb	2·5	300	4·63	294	4·64
IIc[a]	1·25	325	4·84	270	4·84
III[b]	ss	288	—	281	—
IVa	1·25	284	5·00	279	4·99
IVb	1·25	283	4·98	279	4·97
Va	2·5	284	4·60	275	4·59
Vb[c]	1·25	283	4·82	255	5·10
VI	2·5	284	4·78	276	4·79

Cell paths 0·1 mm; [a] additional band at 245 nm (log ε, 5·00); [b] saturated solution; [c] additional band at 255 nm (log ε, 5·10).

Compounds III and IVa exhibit only one absorption band (3180 cm^{-1} and 3185 cm^{-1}, respectively) in pyridine, which shows that in these compounds the $OH\cdots\pi$ conformation is totally absent and only the $OH\cdots N$ intermolecular hydrogen bonding is observed, while compound VII, reported by Cairns and Eglinton,[3] displays only the sharp intense band at 3483 cm^{-1}, demonstrating that the intramolecularly hydrogen bonded conformation is undisturbed in pyridine solution.

Compound IVa was examined in pyridine over a range of temperatures (25 → 80°C). At a temperature higher than 30°C, two bands are observed ν(OH) free, 3625 cm^{-1}, ε_a, 30–60 l $mole^{-1}$ cm^{-1}; ν(OH) bonded, 3185–3215 cm^{-1}, ε_a, 180–120 l $mole^{-1}$ cm^{-1}.

Compound IIc shows in nujol the same well-defined ν(OH) absorption at 3438 cm^{-1} (Table 3) as that observed in solution and the conformation in the crystal is therefore presumed to be the same.

All compounds investigated except those of I and IId were examined in other ways, i.e. by UV and NMR. In the UV all compounds show two or three high-intensity bands (Table 4). The bands are assigned to the π–π^* transitions. The longest wavelength band observed with compound IIc (λ_{max}, 325 nm) also supports strong H-bonding.

Since the rigid conformation involving two intramolecular $OH\cdots\pi$ hydrogen bonds exists at all concentrations examined (0·1 M to 0·25 mM in CCl_4) of the compounds studied, it was possible to detect the chemical shift of the OH proton by NMR. All compounds except those of I, Va, Vb and VI show a single, sharp, concentration-independent signal at $\sim 5{\cdot}2\ \tau$, which on addition of D_2O disappeared after a few minutes. However, from NMR data of the compounds studied we were unable to find further evidence regarding the conformations adopted.

EXPERIMENTAL

IR spectra were recorded with a Perkin–Elmer, Model 225 double beam instrument (polystyrene standard). Wave-number measurements for the free and bonded OH bands are believed to be accurate to ± 1 cm^{-1}. The intensities were measured on bands of not less than 0·05 absorbance. The apparent half-band widths $\Delta\nu_{1/2a}$ are quoted to the nearest integer; where necessary they were determined by reflection of the undisturbed wings of the asymmetrical bands. Intensities are given as apparent molar absorptivities, ε_a, (1 $mole^{-1}$ cm^{-1}) rounded to the nearest 5 units (measured from a superimposed solvent–solvent base.) UV spectra were recorded with a Perkin–Elmer, Model 450 double beam spectrophotometer in cyclohexane. NMR spectra were obtained with a 60 Mc/s BS 744 NMR machine (TMS as internal standard) in CCl_4. The mol wt measurements were made with a VPO Laboratorne pristroje (Czechoslovakia) vapour pressure osmometer precalibrated with benzil in CCl_4 over a wide concentration range in CCl_4. Analar CCl_4 and cyclohexane (spectroscopic grade) were used without further purification. Analar $CHCl_3$ was dried several times by passage through a column of blue silica gel. Pyridine was distilled from KOH. All compounds examined, were of analytical purity, and the physical constants agreed well with the literature.

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