1107. *Hydrogen Bonding in Phenols. Part II.*[1] *Alkyl Substituted Bis(hydroxyphenyl)alkanes (Dinuclear Novolaks)*

By T. Cairns and G. Eglinton

An alkyl substituted bis(hydroxyphenyl) alkane (IIIe) is assigned a unique conformation involving strong OH · · · π intramolecular hydrogen bonds. This conformation is maintained in the solid state and in solution in the solvents examined.

Conformational analysis of a number of polyphenolic compounds of the novolak type [2] has already been the subject of an infrared study.[1] The peculiar effect reported [3,4] in the ν(OH) region of the dinuclear novolaks [bis(hydroxyphenyl)alkanes] fully substituted on the central aliphatic carbon—the appearance of a single, sharp, bonded hydroxyl absorption—has been further investigated and our findings are now described.

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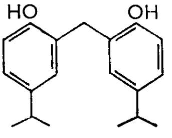
[1] Part I, T. Cairns and G. Eglinton, *Nature*, 1962, **196**, 535.

[2] A. Zinke, R. Ott, and F. H. Garrana, *Monatsh.*, 1958, **89**, 135, and refs. cited therein.

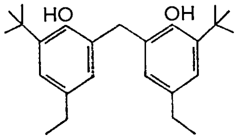
[3] N. D. Coggeshall, *J. Amer. Chem. Soc.*, 1950, **72**, 2836.

[4] R. F. Goddu, *Analyt. Chem.*, 1958, **30**, 2009.

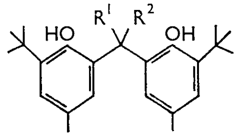
It might be thought that the weaker OH · · · benzene ring [5,6] type of hydrogen bond is unlikely to compete with the normally stronger OH · · · OH type of hydrogen bond, except in unusual steric situations. We now report hydroxyl absorptions in n-hexane, carbon tetrachloride, chloroform, diethyl ether, and pyridine for four novolaks (I), (II), (IIIb), and (IIIe) (Table 1, Figure 1). The data are interpreted in terms of conformational equilibria.



(I)



(II)



(III)

a, $R^1 = R^2 = H$; b, $R^1 = H$, $R^2 = CH_3$; c, $R^1 = H$, $R^2 =$ cyclohexyl; d, $R^1 = H$, $R^2 =$ phenyl; e, $R^1 = R^2 = CH_3$; f, $R^1 = CH_3$, $R^2 = Et$.

EXPERIMENTAL

Measurements.—Spectra were recorded linearly in cm.$^{-1}$ as percentage transmission with a Unicam S.P. 100 double-beam infrared spectrophotometer equipped with an S.P. 130 sodium chloride prism-grating double monochromator [3000 lines per inch (2150—3650 cm.$^{-1}$) and 1500 lines per inch (650—2150 cm.$^{-1}$)] operated under the general procedure described previously.[7] Full spectra of compounds (I), (II), and (IIIe) (3650—650 cm.$^{-1}$) were recorded as KCl discs and will appear in the D.M.S. Index (Butterworths) as card nos. 12950—2. The n.m.r. results were obtained on a Perkin-Elmer model R 10 Spectrometer (60 Mc/sec.). The ultraviolet spectra were obtained on a Unicam S.P. 800B spectrophotometer. The molecular weight of compound (IIIe) in dilute carbon tetrachloride was measured with a Mechrolab vapour pressure osmometer model 301A precalibrated with benzil in carbon tetrachloride. The gas-liquid chromatography results were obtained on a Pye "Argon Chromatograph" using 46 × 0·2 in. columns.

Materials.—Carbon tetrachloride (AnalaR) and n-hexane (spectroscopic grade) were used without further purification. Chloroform (AnalaR) was freed from ethanol by two successive passages through blue silica gel immediately before use. The anhydrous diethyl ether solutions were examined immediately after preparation. Pyridine was dried by distillation from KOH. Compounds (I), II), and (IIIe) were supplied by Dr. Robert F. Goddu [4] of the Hercules Powder Company, compound (IIIb) by Dr. N. D. Coggeshall [3] of the Gulf Research and Development Company, whom we thank. The full n.m.r. spectra were in accord with the structures assigned to these novolaks.

RESULTS AND DISCUSSION

Previously we examined the infrared absorption spectra of a number of polyphenols of novolak type.[1] Our results showed that in carbon tetrachloride these flexible molecules, in which the phenolic nuclei are linked by methylene bridges, assume well-defined conformations involving the OH · · · OH type of intramolecular and intermolecular hydrogen bonds. We now compare four alkyl substituted dinuclear novolaks (I, II, IIIb, and IIIe). Compound (I) is representative of the type of dinuclear novolak discussed in Part I,[1] where it was found that in the absence of *ortho*-substituents OH · · · OH intra-bonding is dominant at low concentrations, but is superseded by dimerisation (involving a complete ring of four hydrogen bonded hydroxyls) at higher concentrations. The *ortho*-disubstituted dinuclear novolak (II) exemplifies the type of heavily hindered phenol for which intermolecular association is difficult, and which permits an assessment of the competing intramolecular situations. In the isomeric, but more heavily *ortho*-disubstituted dinuclear

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[5] A. W. Baker and A. T. Shulgin, *Spectrochim. Acta*, 1963, **19**, 1611.
[6] G. Aulin-Erdtman and R. Sanden, *Acta Chem. Scand.*, 1963, **17**, 1991.
[7] T. Cairns, G. Eglinton, and S. McGeachin, *J.*, 1965, 1235.

novolak (IIIe), the latter situation is further emphasised. The degree of substitution of novolak (IIIb) is of intermediate extent.

Hydrogen Bonding in Novolaks.—Compound (I) (Table 1, Figure 1) shows the presence of three hydroxyl absorptions in CCl_4. Following our previous results,[1] we assign the band at 3476 cm.$^{-1}$ to an intramolecular OH · · · OH hydrogen bond; the presence of an unhindered hydroxyl group at 3611 cm.$^{-1}$ (ε^a approximately equivalent to that for one phenolic OH group) adds support to this assignment. The broad, concentration-dependent, band at 3300 cm.$^{-1}$ is assigned to the closed ring of hydrogen bonds which results from dimeric association in the manner already discussed.[1] In chloroform solution where some interaction with the solvent is to be expected the absorption bands (Table 1, Figure 1) broaden and decrease in frequency and the amount of interbonding is reduced.

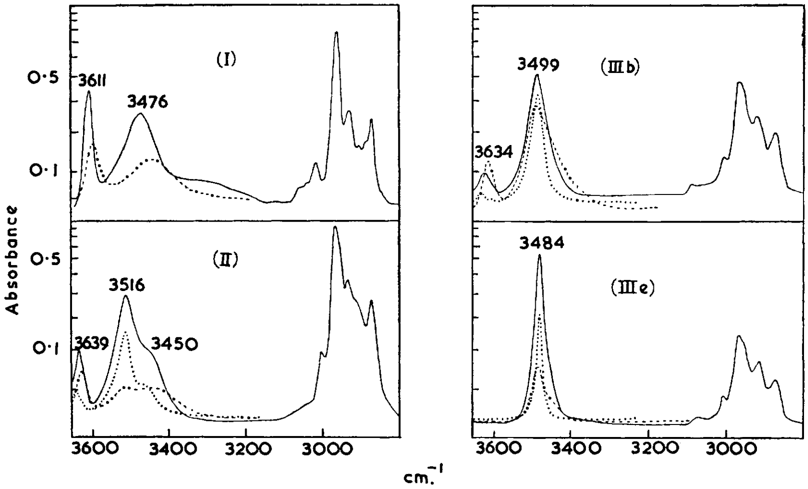


FIGURE 1. Hydroxyl stretching absorptions for solutions of compounds (I), (II), (IIIb), and (IIIe) in n-hexane (· · · ·), carbon tetrachloride (———), and chloroform (– – – –). Frequency values quoted are for CCl_4. Cell paths: n-hexane and $CHCl_3$, 0·5 mm.; CCl_4, 2 cm. Concentrations: (I), CCl_4, 0·97 mM; $CHCl_3$, 3·8 mM: (II), n-hexane, 12·4 mM; CCl_4, 0·87 mM; $CHCl_3$, 2·9 mM: (IIIb), n-hexane, 9·1 mM; CCl_4, 0·93 mM; $CHCl_3$, 2·3 mM: (IIIe), n-hexane, 3·5 mM; CCl_4, 0·3 mM; $CHCl_3$, 3·8 mM

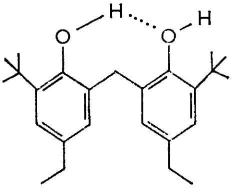
TABLE 1

Hydroxyl stretching absorptions of compounds (I), (II), (IIIb), and (IIIe)

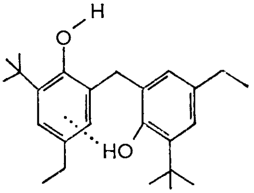
	n-Hexane			CCl_4			$CHCl_3$			
Compound	ν	$\Delta\nu_{\frac{1}{2}}^a$	ε^a	ν	$\Delta\nu_{\frac{1}{2}}^a$	ε^a	ν	$\Delta\nu_{\frac{1}{2}}^a$	ε^a	Assignments
(I)	Insoluble			3611	26	170	3600	40	190	" Free "
				3476	100	125	3450	br	140	OH · · · OH intra
				3300	br	—				OH · · · OH inter
(II)	3647	—	85	3639	32	100	3631	32	165	" Free " hindered
	3620	sh	—	3620	sh	—				Free
	3517	38 *	330	3516	58 *	210	3515	—	85	OH · · · π intra
	3470	sh	100	3450	sh	—	3440	—	85	OH · · · OH intra
(III*b*)	3647	—	25	3634	—	40	3626	18	100	Free hindered
	3500	36	665	3499	50	385	3500	82	245	OH · · · π intra
(III*e*)	3483	15	1650	3484	22	1000	3486	40	630	OH · · · π intra

All absorptions were found to be concentration-independent over the range studied except those for compound (I). Concentrations and cell paths are given in Figure 1. — Not measured. sh, Shoulder. br, Broad. * Half-band width measured by reflection of undisturbed wing.

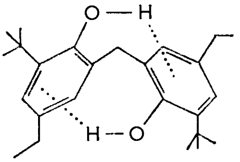
Compound (II) (Table 1, Figure 1) has a more complex spectrum, though introduction of the *ortho*-di-t-butyl groups prevents self-association. The shoulder at 3450 cm.$^{-1}$ (in CCl_4) is assigned to the intramolecular OH · · · OH bond [cf. compound (I) 3476 cm.$^{-1}$]. Support for this assignment is adduced from the presence of the absorptions at 3639 cm.$^{-1}$ (in CCl_4), characteristic of a hindered free hydroxyl group where the OH group is directed towards a t-butyl group (ε^a equivalent to approximately half that for one free hydroxyl [8]). The sharper band at 3516 cm.$^{-1}$ is assigned to an intramolecular OH · · · benzene ring (OH · · · π type) hydrogen bond. Oki and Iwamura [9] have already shown that this sort of bonding situation pertains in *o*-hydroxydiphenylmethane (*o*-benzylphenol), where (in CCl_4) the OH · · · π bond absorbs at 3560 cm.$^{-1}$ with $\Delta\nu_{\frac{1}{2}}^{a} = 56$ cm.$^{-1}$. The unsubstituted phenyl ring is formally more free to rotate than the corresponding heavily substituted benzene ring of compound (II), but the band is about the same width.



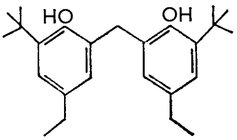
(II,i)



(II,ii)



(II,iii)



(II,iv)

Several conformers may be in equilibrium. Thus for CCl_4, we can suggest (II, i) a conformer involving an intramolecular OH · · · OH hydrogen bond (3450 cm.$^{-1}$) with the " free " hydroxyl group (3639 cm.$^{-1}$) directed towards the *o*-butyl group; (II, ii) a conformer involving an intramolecular OH · · · π hydrogen bond (3516 cm.$^{-1}$) with the other hydroxyl group free, but not necessarily directed towards the *o*-t-butyl group (this would explain the slight shoulder at 3620 cm.$^{-1}$); (II, iii) a conformer involving two similar intramolecular OH · · · π bonds (3516 cm.$^{-1}$); (II, iv) a conformer with both hydroxyls free (3639 and 3620sh cm.$^{-1}$).

The conformer(s) involving the intramolecular OH · · · π type of hydrogen bond is favoured in CCl_4 (according to ε^a). In n-hexane, however, this conformation is more favoured as can be seen by the increased intensity of the band at 3517 cm.$^{-1}$ (Figure 1) at the expense of the other absorption bands. It is interesting that the frequency of this band is practically the same in all three solvents (Table 1). This supports conformer (II, iii) since the π-bonded hydroxyl groups in this conformation would be relatively inaccessible to solvent molecules. This trend of solvent behaviour might be expected on the grounds that non-polar solvents will favour conformations in which alkyl groups are directed towards the solvent cage and polar groups such as hydroxyls are directed into the interior of the molecule. The reverse situation would apply in polar solvents such as $CHCl_3$ and the exposed OH · · · OH arrangement could be directly solvated by chloroform molecules. In summary, therefore, the intramolecular OH · · · π hydrogen bonded conformation(s) of (II) is strongly favoured in n-hexane, but is less favoured in CCl_4 and especially $CHCl_3$, but the exact constitution of the equilibrium mixture remains in doubt.

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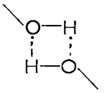
[8] L. J. Bellamy, G. Eglinton, and J. F. Morman, *J.*, 1961, 4762.

[9] M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **1960, 33**, 681, 717.

Compound (IIIb) (Table 1, Figure 1) exhibits only two hydroxyl absorptions in n-hexane, CCl_4, and $CHCl_3$. The high-frequency band, which must correspond to a free hydroxyl directed towards an *ortho*-alkyl group,[8] falls in frequency but increases in intensity on going from n-hexane through CCl_4 to $CHCl_3$. The second band is assigned to an intramolecular OH · · · π hydrogen bond of the type already discussed for compound (II), though the band is shifted to a slightly lower frequency. The intensity data require that the dominant conformer in n-hexane and CCl_4 is the doubly OH · · · π hydrogen bonded system [cf. (II, iii)]. The free hydroxyl absorption must arise from conformer(s) corresponding to (II, ii) and (II, iv).

Finally, compound (IIIe), the most heavily substituted of the four novolaks studied, has a single intense ν(OH) absorption (Table 1, Figure 1). The bulky *ortho*-alkyl substituents prevent intermolecular association at all concentration levels as was fully confirmed by molecular-weight estimation in CCl_4. The molecular weight (vapour pressure method) was found to be 367 ± 5 (theoretical 368). The single narrow absorption band at 3484 cm.$^{-1}$ indicates that both hydroxyls must be similarly hydrogen bonded intramolecularly to the adjacent benzene rings [cf. (II, iii)]. The other possibility would be the arrangement, already suggested by Coggeshall [3] for these compounds, which involves paired hydroxyls (inset). However, such an association seems to have no precedent and is, in any case, sterically impossible without twisting the OH bonds out of the plane of the benzene rings. The narrowness of the absorption band [10] at 3484 cm.$^{-1}$, observed in all solvents, implies a rigid,[9] well-defined complex. The only conformation which seems to fit the data is illustrated in Figure 2. Methyl substitution of the central aliphatic carbon (II → IIIb → IIIe) evidently interferes sterically with the formation of the OH · · · OH intramolecular hydrogen bond. Examination of the Dreiding model of (IIIe) shows that one of these methyl groups rotates into the line of the OH · · · OH intra-bond as the O · · · O distance nears 2·7 Å. On the other hand, these bridge methyls are quite distant in the OH · · · π bonded conformer (Figure 2).



Some data for novolaks of type (III) [including (IIIb) and (IIIe) discussed above] have been recorded by Coggeshall [3] and later Goddu [4] (Table 2). In view of the present results we assign the bonded band in each case to an OH · · · π intramolecular hydrogen bond. From the data in Table 2 it seems that a single bulky substituent such as cyclohexyl (IIIc) is sufficient to enforce complete OH · · · π bonding.

TABLE 2

Literature data [3,4] recorded for hydroxyl stretching absorptions of compounds of type (III)

Compound	R^1	R^2	ν(OH) absorptions in CCl_4		$\frac{\varepsilon \text{ bonded} \,.\, 100}{\varepsilon \text{ free} + \varepsilon \text{ bonded}}$	Ref.
			ν(OH) free	ν(OH) bonded *		
IIIa	H	H	3636	3500	69·7	3
IIIb	H	CH_3	3636	3500	81·7	3
IIIc	H	Cyclohexyl		3480	100	3
IIId	H	Phenyl	3636	3500	92·3	3
IIIe	CH_3	CH_3		3480	100	3, 4
IIIf	CH_3	C_2H_5		3480	100	3

* Assigned to OH · · · π in the present work.

OH · · · π Intramolecular Hydrogen Bonds.—Literature data (in CCl_4) for three OH · · · π intramolecularly bonded compounds [6,9] and our data for compounds (IIIb) and (IIIe) are presented in Table 3. A reference point is provided by West [11] for phenol in benzene as solvent (3564 cm.$^{-1}$; the bonding shift, $\Delta\nu$ = 47 cm.$^{-1}$). We believe that the absorption characteristics displayed by (IIIe) [the bonding shift ($\Delta\nu$ = 163 cm.$^{-1}$), the half-band width ($\Delta\nu_{\frac{1}{2}}^{a}$ = 22 cm.$^{-1}$), and the integrated absorption intensity ($A \times 10^{-4}$ = 9·8)] can only be

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[10] I. Brown, G. Eglinton, and M. Martin-Smith, *Spectrochim. Acta*, 1962, **18**, 1593.
[11] R. West, *J. Amer. Chem. Soc.*, 1959, **81**, 1615.

explained by a particularly well-defined and relatively strongly bonded conformation (Figure 2) with a very limited range of internal movement. It is especially interesting that the total integrated absorption intensities, $A \times 10^{-4}$, per hydroxyl for (IIIb) and (IIIe) are respectively 3 and 4 times that observed for the other compounds.

TABLE 3

Summary of hydroxyl stretching absorptions and integrated absorption intensities for various phenols in CCl_4

Compound	ν	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}	$\Delta\nu$ *	10^4A	Assignment
p-Cresol	3612	17	200	—	1·25	Free
o-Hydroxybiphenyl	3607	18	25	—	0·18	Free
	3565	17	200	46	1·17	OH · · · π intra
2,2′-Dihydroxybiphenyl	3599	18	55	—	0·30	Free
	3554	19	390	57	2·28	OH · · · π intra
o-Hydroxydiphenylmethane †	3611	17		—	0·87	Free
	3560	56		51	0·80	OH · · · π intra
(IIIb)	3634	—	40	—	0·25	Free
	3499	50	385	148	6·90	OH · · · π intra
(IIIe)	3484	22	1000	163	9·80	OH · · · π intra

All samples examined in 2 cm. cells (*ca.* 0·01M). Areas calculated according to Ramsay's method.[12]

* $\Delta\nu = \nu$(OH) free $-$ ν(OH) bonded. The value for ν(OH) free has been taken as 3611 cm.$^{-1}$ except for (IIIb) and (IIIe) where the value of 2,6-di-t-butylphenol (3647 cm.$^{-1}$) has been adopted. † Results taken from ref. 9. In this ref. Oki and Iwamura quote a value of 0·20 and 1·28 for $10^{-4}A$ for the free and bonded hydroxyl absorptions of *o*-hydroxybiphenyl respectively.

To test the stability of this rigid conformation adopted by compound (IIIe) all four novolaks (I, II, IIIb, and IIIe) have been examined in basic solvents. In diethyl ether (Table 4) compounds (I), (II), and (IIIb) exhibited very broad bands centred around 3350 cm.$^{-1}$ as expected for OH · · · $O(Et)_2$ intermolecular association,[8] though in the case of compound (IIIb) the 3484 cm.$^{-1}$ band remained to some extent. Compound (IIIe), however, showed only the sharp intense band at 3483 cm.$^{-1}$, demonstrating that the intramolecularly hydrogen bonded conformation (Figure 2) is undisturbed in solution in diethyl ether. Again, when compounds (IIIb) and (IIIe) were examined in pyridine, which is much more basic than diethyl ether, compound (IIIb) exhibited a very broad band as expected for OH · · · NC_5H_5, *i.e.*, OH · · · π conformation broken, while compound (IIIe) still showed a band at 3482 cm.$^{-1}$. It is quite remarkable that the intra-bonded conformation is undisturbed in a solvent which is such a good acceptor for hydrogen bonding,

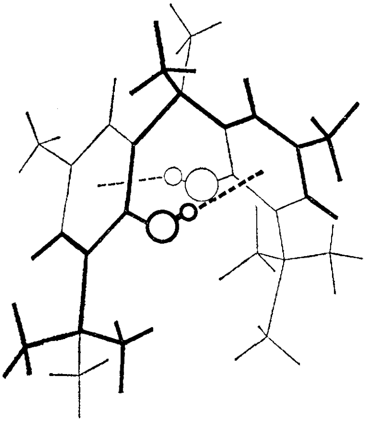

FIGURE 2. Planar projection of the Dreiding molecular model of the single conformation assigned to compound (IIIe). The large and small circles indicate the oxygen and hydrogen atoms of the hydroxyl groups respectively. The dotted lines indicate the hydrogen bonds. The front edge of the molecule is depicted by heavy lines

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[12] N. D. Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

and it is the introduction of the second methyl group which seems to be important. However, the increased half-band width ($\Delta\nu_{\frac{1}{2}}^{a} = 65$ cm.$^{-1}$) for (IIIe) as compared with that in ether ($\Delta\nu_{\frac{1}{2}}^{a} = 24$ cm.$^{-1}$) can be explained by some slight degree of interaction with neighbouring pyridine molecules.

The spectra of (IIIe) in the solid state (KCl disc) and in solution (CCl_4) were virtually superposable over the regions examined (3650—1600 and 1500—1000 cm.$^{-1}$). Compounds (I), (II), and (IIIb), however, exhibited marked differences, especially in the fingerprint region (new bands and differences in relative intensities). The conformation of (IIIe) in the crystal is therefore presumed to be the same as that assigned from solution data (Figure 2).

TABLE 4

Hydroxyl stretching absorptions for compounds (I), (II), (IIIb), and (IIIe) in diethyl ether and pyridine

Solvent	Compound	Molarity	ν	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}	Assignment
Diethyl ether	(I)	0·13	(3350)	br	—	$OH \cdots O(Et)_2$
	(II)	0·10	(3350)	br	—	$OH \cdots O(Et)_2$
	(IIIb)	0·05	3484	—	160 *	$OH \cdots \pi$ intra
			(3300)	br	—	$OH \cdots O(Et)_2$
	(IIIe)	0·04	3483	24	1070	$OH \cdots \pi$ intra
Pyridine	(IIIb)	0·04	(3200)	br	—	$OH \cdots NC_5H_5$
	(IIIe)	0·06	3482 †	65	800	$OH \cdots \pi$ intra

Cell thickness 0·05 mm.
Values in parenthesis are approximate.

* Apparent peak height used without subtraction of contribution from overlapping 3300 cm.$^{-1}$ band. † There is extensive broadening at the base of the peak which may correspond to a little intermolecular association, $OH \cdots NC_5H_5$.

We have attempted with only limited success to find further evidence bearing on the conformation adopted by compound (IIIe) by examining the molecule in other ways (n.m.r., ultraviolet, and g.l.c.). Since this rigid conformation involving two intramolecular $OH \cdots \pi$ hydrogen bonds exists at all concentrations examined (0·1M to 0·3mM in CCl_4) it was possible to determine the chemical shift of the hydroxylic proton in this conformation by n.m.r. It was found to be a single, sharp, concentration-independent, signal at 5·1 tau. Addition of D_2O caused this signal to disappear slowly during a few minutes. [It is difficult to draw comparisons with other $OH \cdots \pi$ intra-bonded molecules since they usually require to be recorded at very low levels of concentration to ensure no interbonding.] We were unable to find any marked differences in the ultraviolet spectra for compound (IIIe) and other phenols under conditions (cyclohexane) paralleling the infrared measurements in n-hexane. Phenols exhibit a high-intensity band around 270 mμ which is assigned to a $\pi \longrightarrow \pi^*$ transition. Both 2,6-di-t-butyl-4-methylphenol and compound (I) have twin peaks in this region—278 and 284 mμ ($\varepsilon = 2000$) and 280 and 285 mμ ($\varepsilon = 4650$), respectively. On the other hand, however, compounds (II) and (IIIe) each have a single flat-topped peak [285 mμ ($\varepsilon = 4650$) and 284 mμ ($\varepsilon = 5100$), respectively]. Coggeshall,[3] however, has found marked variations in the degree of ionisation of the different novolaks in solvents containing dissolved base. Compound (II) ionises readily whereas compound (IIIe) undergoes very little ionisation [*i.e.*, less acidic than (II)]. This information is in keeping with the conformation assigned to compound (IIIe) (Figure 2) where the hydroxyls are protected by steric congestion. The comparative shielding from the environment experienced by the phenolic groups in compound (IIIe) is further illustrated by the g.l.c. data reported in Table 5. Compound (II), which is isomeric with (IIIe) but possesses much more exposed phenolic hydroxyls, shows a more than three-fold increase in retention time on changing from the non-polar hydrocarbon phase (Apiezon L) to the highly polar polyester phase (*NN*-di-p-hydroxyethyl)aniline succinate. By contrast, compound

TABLE 5

Retention times for compounds (II) and (IIIe)

Column conditions	Compound	R_t (min.)
0·5% Apiezon L at 175°c and 30 ml./min.	n-Docosane ($C_{22}H_{46}$)	7·8
	(II)	20·3
	(IIIe)	9·05
2% *NN*-di-(2-hydroxyethyl)aniline succinate at 175°c and 20 ml./min.	n-Octacosane ($C_{28}H_{58}$)	14·05
	(II)	72·50
	(IIIe)	9·05

(IIIe) under the same conditions has the same retention time on both phases: such behaviour is in keeping with inhibition of hydrogen bonding between the phenolic hydroxyls of the solute molecules and the basic sites of the polar phase.

Solvent-dependence of Conformations of Dinuclear Novolaks.—The alkyl substituted bis(hydroxyphenyl)alkanes (I), (II), (IIIb), and (IIIe) illustrate in rather a clear way how progressively increasing steric congestion can affect the conformations of molecules and their ability to associate intermolecularly with other molecules of the same type or with those of the solvent. Thus (*a*) The lightly substituted bis(hydroxyphenyl)alkane (I) associates tenaciously to form a ring of four hydrogen bonds (3200 cm.$^{-1}$ in CCl_4).[1] In very dilute solution the conformation of the monomer involves a fairly strong OH · · · OH intramolecular hydrogen bond (3476 cm.$^{-1}$ in CCl_4); (*b*) Introduction of twin bulky *ortho*-alkyl substituents (II) prevents self-association but not association with basic solvent molecules, such as ether or pyridine. In solvents such as n-hexane, carbon tetrachloride, and chloroform the monomer is present as more than one conformer and these involve OH · · · π intra-bonds as well as OH · · · OH. The least polar solvents (n-hexane $>$ CCl_4 $\gg$ $CHCl_3$) favour the conformers having OH · · · π bonds; (*c*) A single methyl substituent (IIIb) on the central aliphatic carbon greatly increases the dominance of the conformer(s) involving OH · · · π intra-bonds but the hydroxyls are still capable of association with basic solvents. One remarkable feature is the conformational control exercised by the solvent. In n-hexane compound (IIIb) must be almost entirely in the completely bonded OH · · · π conformation [cf. (II, iii)]; in $CHCl_3$ the proportion of conformer(s) with a free hydroxyl is greatly increased at the expense of the OH · · · π intra-bonded conformation; in CCl_4 the effect is intermediate; (*d*) Introduction of the final methyl substituent (IIIe) forces the molecule to adopt a single very restricted conformation (Figure 2) having two identical OH · · · π intramolecular hydrogen bonds (3484 cm.$^{-1}$ in CCl_4). The hydroxyls are buried within the molecule and their stretching frequencies, ν(OH), are almost unaffected by even strongly basic solvents.

Finally, the spectrum of compound (IIIe) in the solid state shows the same well-defined ν(OH) absorption at 3484 cm.$^{-1}$ as in solution and the conformation in the crystal is therefore presumed to be the same as that observed in solution. We look to support for our conclusions concerning the "narcissistic" conformation of compound (IIIe) from an *X*-ray analysis of a suitable heavy-atom derivative. Such a spiral conformation is formally capable of optical resolution provided the strength of the two intramolecular hydrogen bonds is sufficient to maintain the conformation under the conditions employed in the attempted resolution. Should this prove to be so we believe that this molecule, or a suitable derivative, would be the first example of optical activity where asymmetry is largely maintained by intramolecular hydrogen bonding.

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