Hydrogen bonding in phenols. IX.* The synthesis and the OH $\cdots \pi$ intramolecular hydrogen bonding of alkyl-substituted 2-hydroxydiphenylmethanes

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The synthesis of 2-hydroxy-X′-diphenylmethanes, where X′ = H, 4-CH_3, 4-C_2H_5, 4-$CH(CH_3)_2$, 4-$C(CH_3)_3$. 2,4,6-tri(CH_3), 2,3,5,6-tetra(CH_3), 2,3,4,5,6-penta(CH_3), is described. The OH$\cdots\pi$ intramolecular hydrogen bonding of the above-mentioned compounds in CCl_4 solution is studied by infrared spectroscopy. Energies of the hydrogen bonding were found to increase with the increasing number of alkyl groups on the aromatic ring and they linearly correlate with the ionization potentials of the appropriate alkyl benzenes.

2-Hydroxydiphenylmethanes were prepared by benzylation of sodium phenolates in an anhydrous medium. The reaction mixture contained also 4-hydroxydiphenylmethane and benzyl phenyl ether [1]. Hydroxydiphenylmethanes so far known were prepared by this method; they are used in practice as antioxidants [2] or biologically active compounds [3—8].

Intramolecular hydrogen bonding of 2-hydroxydiphenylmethane was investigated by *Oki* and co-workers [9] and *Baker et al.* [10]. As known, some dihydroxydiphenylmethanes and dihydroxydiphenyl sulfides form relatively strong OH $\cdots \pi$ hydrogen bonds [11—14].

This paper was aimed to study the dependence of the energy of the OH $\cdots \pi$ intramolecular bonding on both the nature and the number of alkyl groups attached to the aromatic ring.

Experimental

Alkyl-substituted 2-hydroxydiphenyl methanes (I—VIII)

A suspension of NaH (1 mole) in a water-free toluene (150 ml) was gradually added to a solution of phenol (1 mole) in a hot anhydrous toluene under stirring and passing a stream of dry nitrogen through the reaction mixture. Then, the respective alkyl-substituted benzyl chloride (1.1 mole) was added to the boiling stirred suspension. Stirring and heating was continued for 5 hrs whereupon the reaction mixture was cooled and acidified with hydrochloric acid. The toluene layer was separated and washed with $NaHCO_3$ solution and water. Reaction products containing phenolic group were allowed to react with a 40% aqueous-methanolate solution of NaOH (Claisen solution) to yield sodium phenolates. The toluene layer was removed, phenolic compounds were liberated with hydrochloric acid and extracted with ethyl ether. The crude product, obtained

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* For Part VIII see *Tetrahedron* ***29***, 1825 (1973).

after drying and removal of the solvent, was distilled under reduced pressure. The first fraction contained the unchanged components, the second mostly 2- and 4-hydroxydiphenylmethanes, whilst the residue consisted of more benzylated phenols.

Separation of 2- and 4-hydroxydiphenylmethanes from their mixture

To a boiling solution of $Ba(OH)_2 \cdot 8H_2O$ (0.75 mole) in water (900 ml) the mixture to be separated (1 mole) was added and heated for 15—30 min at the boiling-point temperature. The white barium salt of 4-hydroxydiphenylmethane precipitated after cooling was filtered; the well water-soluble barium salt of 2-hydroxydiphenylmethane was acidified with hydrochloric acid and extracted with ether. The crude products were purified by distillation and crystallization or by chromatography over alumina.

Alkyl-substituted 2-hydroxydiphenylmethanes thus prepared are listed in Table 1.

Infrared spectra of substances under investigation were measured with a Unicam SP 100 G apparatus in 1-cm cells within 3100 and 3650 cm^{-1}; concentration 2.2 to 4.5×10^{-3} M. The studied compounds did not form intermolecular hydrogen bonds in the given concentration range. The wavenumber scale was calibrated by means of the water-vapour spectrum in the $\sim 3600\ cm^{-1}$ region accurate to $\pm 0.1\ cm^{-1}$. The wavenumber reading was accurate to $\pm 0.5\ cm^{-1}$. Carbon tetrachloride (spectroscopic grade) was dried several times by passing it through a silica gel column.

Results and discussion

Of those listed in Table 1, only compounds *I* [9] and *IV* [1] have been reported. The low yields are mostly due to the concurrent formation of 4-hydroxy-X′-diphenylmethane, the separation of which was in most cases considerably difficult.

Table 1

2-Hydroxy-X′-diphenylmethanes

Compound	X′	Formula	*M*	Calculated/ /found % C	Calculated/ /found % H	Yield [%]	M.p. [°C] B.p. [°C/Pa]
I	H	$C_{13}H_{12}O$	184.23	84.75	6.57	32	171—173/1733
				84.90	6.40		
II	4-CH_3	$C_{14}H_{14}O$	198.26	84.81	7.12	17.5	73— 76/6.66
				84.63	6.98		
III	4-C_2H_5	$C_{15}H_{16}O$	212.30	84.87	7.60	24.5	138—139/13.33
				84.50	7.43		
IV	4-$CH(CH_3)_2$	$C_{16}H_{18}O$	226.32	84.92	8.02	12.8	139—142/13.33
				84.78	8.10		
V	4-$C(CH_3)_3$	$C_{17}H_{20}O$	240.35	84.96	8.39	15.9	144—146/8
				84.80	8.30		
VI	2,4,6-tri-CH_3	$C_{16}H_{18}O$	226.32	84.92	8.02	25.2	128—132/13.33
				84.75	8.10		
VII	2,3,5,6-tetra-CH_3	$C_{17}H_{20}O$	240.35	84.96	8.39	13.8	117—120[a]
				84.91	8.21		
VIII	2,3,4,5,6-penta-CH_3	$C_{18}H_{22}O$	254.38	84.99	8.72	18.2	260—265[a]
				84.83	8.68		

a) Crystallized from light petroleum.

Table 2

Infrared spectral data of compounds examined (in CCl_4)

Compound	Concentration [mM]	ν(OH)						$\Delta\tilde{\nu}$	E
		free			bonded (OH $\cdots\pi$)				
		$\tilde{\nu}_0$	$\Delta\nu_{1/2}$	ε	$\tilde{\nu}$	$\Delta\nu_{1/2}$	ε		
I	4.465	3611	19.2	186	3564	65.5	41	46.5	3.76
II	4.176	3612	19.0	178	3551	63.2	41	60.5	4.89
III	2.473	3612.5	18.2	183	3550	61.2	37	62.5	5.02
IV	2.640	3612.5	18.5	179	3548.5	58.6	37	64	5.19
V	2.213	3612.5	18.2	203	3541	37.4	44	71.5	5.77
VI	2.750	3611.5	17.2	207	3501	44.0	44	110.5	8.95
VII	3.060	3610.5	17.1	187	3491	45.3	35	119.5	9.62
VIII	2.435	3614.5	17.1	185	3477	45.2	44	137.5	11.12

$\tilde{\nu}$, $\Delta\nu_{1/2}$, and $\Delta\tilde{\nu}$ given in cm^{-1}; ε in $l\ mol^{-1}\ cm^{-1}$; E in $kJ\ mol^{-1}$.

The infrared spectra of compounds *I—VIII* (Table 2) revealed two intense bands in the 3480 to 3615 cm^{-1} region. The band at the higher wavenumber was assigned to the stretching vibration of the free hydroxyl group, whereas that at lower wavenumber to the stretching vibration of the hydroxyl involved in the (OH $\cdots\pi$) hydrogen bonding. The increasing number of alkyl groups was associated with the decrease of the half band width $\Delta\nu_{1/2}$ both of free and bonded OH bonds ($\Delta\nu_{1/2} = 19.2 \rightarrow 17.1\ cm^{-1}$ and $65.5 \rightarrow 45.2\ cm^{-1}$, respectively) indicating thus the well defined OH $\cdots\pi$ bonds. Evidently, the equation suggested by *Huggins* and *Pimentel* [15] ($\Delta\nu_{1/2} = 0.72 \cdot \Delta\tilde{\nu} + 2.5$, where $\Delta\tilde{\nu}$ stands for the difference between the wavenumber of the free and bonded OH group) could not be employed for calculation of the half band width of the bonded OH bonds $\Delta\nu_{1/2}$. Similarly, the increase of the electron-donating power of the aromatic ring by alkyl groups resulted in the enhanced difference between the wavenumber of the free ($\tilde{\nu}_0$) and bonded ($\tilde{\nu}$) OH groups ($\Delta\tilde{\nu} = 46.5 \rightarrow 137.5\ cm^{-1}$) this being evaluated when calculating energies of the hydrogen bond in the systems examined. The *Badger* equation [16] with the constant of proportionality 3.4×10^{-3}, found basing upon the intermolecular OH

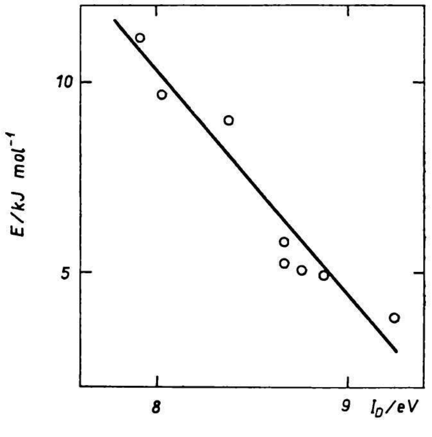

Fig. 1. The dependence of the energy of the OH $\cdots\pi$ intramolecular hydrogen bonding in alkyl-substituted 2-hydroxydiphenylmethanes upon the ionization potentials of alkyl benzenes.

$\cdots\pi$ band measurements of phenol with alkyl benzenes [17, 18], was used to calculate the energy of the OH $\cdots\pi$ bond. Energies of OH $\cdots\pi$ intermolecular hydrogen bonding correlate with ionization potentials of alkyl benzenes [19]. A linear correlation ($r = 0.96$; Fig. 1) between energies of intramolecular hydrogen bonding was found in compounds *I—VIII* and ionization potentials of the proper alkyl benzenes.

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