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HYDROGEN BONDING IN PHENOLS—XI[1]

INTRAMOLECULAR HYDROGEN BONDS IN 2-HYDROXY-R'-DIPHENYLMETHANES

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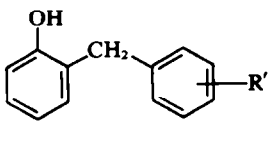
Abstract—The ν(OH) bands of a series of 2-hydroxy-R'-diphenylmethanes (R' = H, 4'-Me, 4'-Et, 4'-CH(Me$_2$), 4'-C(Me$_3$), 2',4',6'-three Me, 2',3',5',6'-tetra Me and 2',3',4',5',6'-penta Me) have been studied over a range of temperatures. Enthalpies ($\Delta H°$) and entropies ($\Delta S°$) of interaction were estimated from the temperature dependencies of equilibrium constants. The positive values of $\Delta H°$ were found with compounds containing a Me group in *ortho*-positions suggesting that π-associated conformers are less favoured than the free conformers.

It is known that in the absence of steric inhibition in the formation of H- bonding the enthalpy of interaction generally increases with the acidity of the OH group as well as with the basicity of the proton acceptor group.[2] Intramolecular H- bonds of the OH ... π type are in general weaker than those of the OH ... O or OH ... N types.[3,4] Therefore, π-electron acceptors yield small values of $-\Delta H°$, $-\Delta S°$ and $-\Delta G°$. The $-\Delta S°$ values for intermolecular H-bonds are of the order of 10–25 e.u. and for intramolecular H-bonds they are smaller. Little is known of the sign of the enthalpies and entropies of the intramolecular interaction between the OH group and proton acceptor groups. The sign of these thermodynamic quantities are usually observed to be negative pointing out that the intramolecular interaction between the proton donor group and the proton acceptor group is an exothermic reaction, i.e. the bonded conformer is more stable than the nonbonded one. The negative values of $\Delta S°$ point to a higher order of the bonded conformer than that in the nonbonded one and *vice versa.*

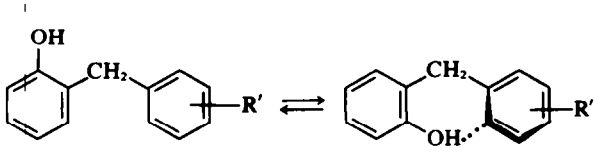
The present work reports intramolecular H-bonding of the OH ... π type. The spectral data of the compounds studied are interpreted in terms of conformational equilibria. In this work we have examined eight phenols where intramolecular interaction of the OH ... π type is present:



R'
H, (1)
4'-Me (2)
4'-Et (3)
4'-CH(Me$_2$) (4)
4'-C(Me$_3$) (5)
2',4',6'-three Me (6)
2',3',5',6'-tetra Me (7)

RESULTS AND DISCUSSION

The compounds studied form intramolecular H-bonds of the OH ... π type. With these compounds two conformers may be in equilibrium:



All compounds studied display two temperature-dependent bands in the OH region in CCl_4 (Table 1). With increasing tempreature the wavenumbers of both free and bonded OH groups slightly increase and the total integrated absorption intensities decrease. These effects were observed by Liddel and Becker[5] with intermolecular H-bonds of methanol in CCl_4 and may be due to a weak H-bonding to the solvent or to a lessening of the dipole-dipole interaction between phenols and solvent molecules by their thermal motion.[6] Enthalpies of interaction $\Delta H°$ together with $\Delta S°/R - \ln a$ are listed in Table 1 and they are smaller than those of the ordinary H-bonding of the OH ... O or OH ... N type. Therefore, these thermodynamic values of interaction may be the best criterion for differentiation of the OH ... π *type of interaction from the ordinary H-bonding. Only compound* **1** *has been studied previously*[2,3] *and its* $\Delta H°$ *is in good agreement with the reported*[2] *value* ($-\Delta H° = 0{\cdot}12 \pm 0{\cdot}05$ kcal/mole) but differs significantly from the reported[4] value $-\Delta H° = 0{\cdot}33 \pm 0{\cdot}05$ kcal/mole. $\Delta H°$ values calculated according to the Badger relation[7] are in general higher than those obtained from the plots of log K against 1/T and they are included in Table 1 for comparison. These values do not reflect the fact that the amount of bonded conformers in compounds **6–8** in a equilibrium increases with the increasing temperature. Therefore, this relation can not be applied to the compounds studied. It is necessary to take into account the rotational degree of freedom. In all compounds studied a loss of energy may be caused by the formation of the internal interaction because the molecule must take the sterically unfavoured structure. In order to interact with the π-electrons, the OH group must be rotated at least partly out of the plane of the aromatic nucleus, thus requiring the loss of resonance energy. Enthalpies of interaction with compounds **1-5** were found to increase systematically with increasing alkyl substitution ($-\Delta H° = 0{\cdot}12 \rightarrow 1{\cdot}0$ kcal/mole) which is in accord with the proton acceptor power of the alkyl substituted aromatic nucleus.

Table 1. IR spectral data and thermodynamic quantities for 2-hydroxy-R'-diphenylmethanes

Compound	ν_0[a]	$\Delta\nu$[a]	$\Delta H°$ [kcal . mol^{-1}]	$\Delta S°/R - \ln a$ [e.u.]	$\Delta H°$[b] [kcal . mol^{-1}]	log K[a]
1	3611·0	46·5	−0·12 ± 0·05	−0·04 ± 0·14	−0·90	0·0207
2	3612·0	60·5	−0·20 ± 0·13	−0·06 ± 0·22	−1·17	0·0508
3	3612·5	62·5	−0·49 ± 0·04	−0·22 ± 0·07	−1·20	0·0643
4	3612·5	64·0	−0·70 ± 0·1	−0·2 ± 0·21	−1·24	0·1267
5	3612·5	71·5	−1·0 ± 0·13	−0·40 ± 0·24	−1·38	0·1429
6	3611·5	110·5	+2·4 ± 0·14	+1·0 ± 0·26	−2·14	−0·3297
7	3610·5	119	+2·6 ± 0·3	+1·2 ± 0·60	−2·30	−0·303
8	3614·5	137·5	+2·6 ± 0·1	+1·1 ± 0·16	−2·66	−0·3274

[a]The values are for 25°.
[b]Calculated according to the relation: $\Delta H° = \Delta\nu/\nu_0\ 1{\cdot}43 \times 10^{-2}$.

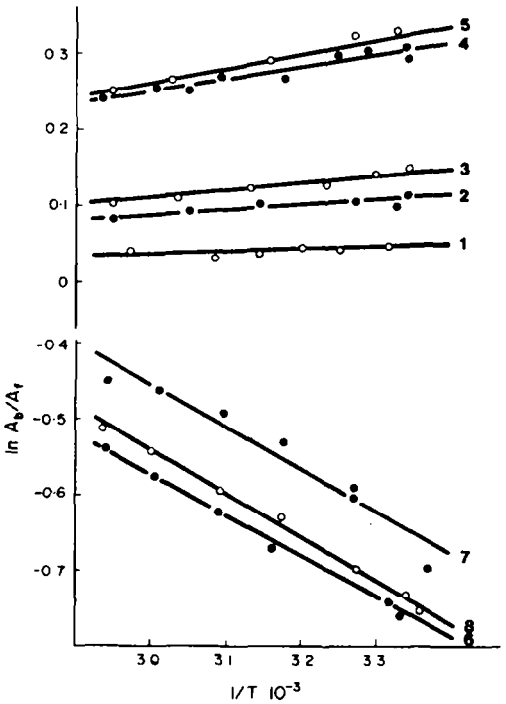


Fig. 1. A plot of ln A_b/A_f vs 1/T of compounds 1-8.

The rotational degree of freedom with theses compounds can be considered to be the same while the alkyl substituent is in position 4 of the aromatic nucleus. With compounds **6–8** steric interactions are sufficiently large to invert the sign of the OH interaction with π-electrons. Positive values of $\Delta H°$ point out that π-bonded conformers are less favoured than the nonbonded ones. The almost equal $\Delta H°$ and $\Delta S°/R - \ln a$ values point out that the OH interaction with π-electrons in compounds **6–8** is approximately the same. The $\Delta S°/R - \ln a$ constant can be assumed to be a measure of the entropy change. Entropy changes with the intramolecular OH ... π interaction of compounds studied are estimated to be in the range of 0·04–1·2 e.u.

EXPERIMENTAL

IR spectra were recorded with a Unicam S.P. 100 G instrument. Wavenumber measurements for the free and intrabonded OH bands are believed to be accurate to ±1 cm^{-1}. The intensities were measured on bands of not less than 0·05 absorbance. To obtain enthalpies and entropies of interaction, measurements were carried out at room and at several other temps up to 67° in 10·0 mm cells, at a concentration range of $2{\cdot}2 \times 10^{-3} \rightarrow 4{\cdot}5 \times 10^{-3}$ M in CCl_4. At this concentration compounds studied do not form intermolecular H-bonding. The temp of the sample soln was measured by a calibrated thermometer inserted in the cell, and was believed accurate to within ±0·5°. Heating was by water from an ultrathermostat. The variation in the thickness of the cell with temps was neglected. The absorption of the solvent was compensated by another cell of the same thickness containing the solvent. Equilibrium constants were calculated from the equation, $K = A_b \cdot a_b/A_f \cdot a_f$ where A_b, A_f are integrated absorption intensities of the ν(OH) bonded and free bands and a_b, a_f represent intensities per molecule with a bonded OH group and a free one, respectively. It has been assumed that the ratio of a_b/a_f is independent of temp while the temp range is small. Integrated absorption intensities of the two bands were calculated according to Ramsay's method,[8] $A = (K/c.d)\ 2{\cdot}303 \log (I_0/I)_{max} \cdot \Delta\nu_{1/2}$. Bands separation was made according to ref 9. Calculations were performed by a Hewlett Packard 9100 B programme calculator. From the plots of log K against 1/T, $\Delta H°$ and $\Delta S°$ were determined by the relation $\ln K = -\Delta H°/RT + \Delta S°/R - \ln a$. It is assumed that the standard enthalpy $\Delta H°$ and entropy $\Delta S°$ of formation of the H bond are independent of temp. Analar CCl_4 was purified according to a general procedure. The compounds used in the investigation were chromatographically pure and their preparation was described previously.[10]

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