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# HYDROGEN BONDING IN PHENOLS—VI[1]

## ABNORMALLY PERSISTENT INTERMOLECULAR ASSOCIATION OF SOME *META*- AND *ORTHO*- SUBSTITUTED PHENOLS AND 2-HYDROXY-8-ACETYL NAPHTHALENE

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**Abstract**—IR, UV, NMR data and osmometric measurements of average molecular weights demonstrate a strong self-association for 2-hydroxy benzalacetone, methyl coumarate, n-propyl coumarate and 2-hydroxy-8-acetyl naphthalene in $CCl_4$ and $CHCl_3$ solutions. All measurements reveal that in these compounds dimeric association is dominant, in which the two H-bonds are in the geometrically favourable 16-membered rings. Using an empirical relation between the concentration of phenols and the intensity of the OH stretching vibration band, the association constants have been determined over the temperature range 20–53°C. Thus, the enthalpies ($-\Delta H^\circ$) and entropies ($-\Delta S^\circ$) for 2-hydroxy-8-acetyl naphthalene, n-propyl coumarate and methyl coumarate have been calculated.

ALTHOUGH phenols are known to associate in non polar media by hydrogen-bonding, the aggregates so formed have no great stability.[2,3] However, some *m*-nitro and *m*-methoxyphenols reported by Anet and Muchowski[4] and *m*-hydroxy acetophenone, ethyl coumarate and bis-(1-hydroxy-4-methyl-phenyl)-methane, reported in our previous work,[3] strongly associate. We have encountered several types of phenolic compounds where intermolecular association, presumably dimeric, is unusually persistent. We have used, whenever possible, three spectral methods—IR, UV and NMR spectroscopy in conjunction with osmometric measurements of average molecular weight.

In the present study the self-association of phenolic compounds is compared with that of substituted anilines as intermediates obtained by the synthesis of model phenolic compounds. In our previous work[3] it was reported that the strong self-association observed with ethyl coumarate is due to the extended conjugated system enticing us to find other strongly associated compounds of a similar type. 2-Hydroxy-8-acetyl naphthalene is an example, it is being discussed in more detail and compared with other phenolic compounds under study. Eleven variously substituted phenols have been examined including three anilines bearing an electron-rich substituent in the *m*- and *o*-positions to the phenolic or amino group as follows. They are: ethyl 3-hydroxy-4-methyl-benzoate I; 3-hydroxy-4-methyl acetophenone II; 3-hydroxy-benzophenone III; 3-hydroxy-4-methyl benzonitrile IV; methyl coumarate V; n-propyl coumarate VI; 2-hydroxy benzalacetone VII; 2-hydroxy-8-acetyl naphthalene VIII; 3-amino-4-methyl acetophenone IX; 3-amino-benzophenone X and 2-amino-8-acetyl naphthalene XI.

TABLE 1. HYDROXYL AND CARBONYL ABSORPTIONS OF m- AND C-SUBSTITUTED PHENOLS IN $CCl_4$

| Compound No. | Conc. (mM) | Cell paths (mm) | $\nu$(OH) | | | | | | Cell paths (mm) | $\nu$(CO) | | | | | | K l/mole |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Free | | | Bonded | | | | Free | | | Bonded | | | |
| | | | $\nu$ | $\Delta\nu_{\frac{1}{2}a}$ | $\varepsilon_a$ | $\nu$ | $\Delta\nu_{\frac{1}{2}a}$ | $\varepsilon_a$ | | $\nu$ | $\Delta\nu_{\frac{1}{2}a}$ | $\varepsilon_a$ | $\nu$ | $\Delta\nu_{\frac{1}{2}a}$ | $\varepsilon_a$ | |
| I | 10 | 2·74 | 3606 | 23 | 100 | 3439 | 78 | 120 | 0·96 | 1722 | 17 | 405 | 1695 | 13 | 415 | 264 |
| | 5 | 5·28 | 3606 | 22 | 120 | 3439 | 77 | 95 | 2·74 | 1722 | 16 | 485 | 1695 | 14 | 325 | 267 |
| | 2 | 9·93 | 3605 | 22 | 155 | 3436 | 76 | 60 | 5·28 | 1722 | 16 | 560 | 1695 | 14 | (250) | 257 |
| | 0·4 | 50·30 | 3606 | 22 | 180 | 3435 | — | (35) | 9·93 | 1720 | 16 | 675 | 1695 | — | (140) | — |
| II | 10 | 2·74 | 3603 | 24 | 90 | 3440 | 78 | 135 | 0·96 | 1687 | (13) | 315 | 1673 | (11) | (480) | 375 |
| | 5 | 5·28 | 3603 | 23 | 105 | 3439 | 77 | 110 | 2·74 | 1687 | (13) | 365 | 1673 | (11) | (435) | 374 |
| | 2 | 9·93 | 3603 | 24 | 130 | 3438 | 78 | 75 | 5·28 | 1688 | (12) | 445 | 1673 | (11) | (350) | 375 |
| | 0·5 | 50·30 | 3605 | 23 | 175 | 3438 | 79 | 35 | 7·06 | 1688 | (11) | 480 | 1673 | — | (320) | 370 |
| | 0·25 | 50·30 | 3604 | 24 | 165 | 3434 | - | (30) | 9·93 | 1688 | (11) | 525 | 1673 | — | (280) | — |
| III | 3 | 9·93 | 3602 | 19 | 185 | 3440 | 110 | 50 | 5·28 | 1665 | 15 | 400 | 1650 | sh | - | 114 |
| | 0·4 | 50·30 | 3602 | 22 | 210 | 3440 | — | (25) | - | — | — | - | — | — | — | - |
| IV | 4·0 | 5·28 | 3601 | 25 | 130 | 3368 | 155 | 40 | | | | | | | | 96 |
| | 2·0 | 9·93 | 3601 | 24 | 160 | 3366 | 150 | 22 | | | | | | | | 82 |
| | 0·4 | 50·30 | 3601 | 25 | 175 | 3390 | 153 | — | | | | | | | | — |

Table 1. (*continued*)

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| V | 5·0 | 9·93 | 3601 | 23 | 96 | 3305 | 250 | 65 | 2·74 | 1719 | 20 | 310 | 1688[a] | (22) | 310 | 222 |
| | 2·5 | 20·0 | 3601 | 24 | 109 | 3302 | 245 | 47 | 5·23 | 1719 | 21 | 388 | 1688[a] | (28) | 257 | 222 |
| | 0·6 | 20·0 | 3600 | 22 | 150 | (3302) | — | (10) | 5·23 | 1718 | 19 | 486 | (1688)[a] | — | (15) | — |
| VI | 20 | 2·74 | 3603 | 25 | 56 | 3300 | 250 | 114 | 0·5 | 1715 | (26) | 264 | 1687[b] | (22) | 516 | 309 |
| | 4 | 9·93 | 3603 | 25 | 105 | 3300 | 250 | 72 | 2·74 | 1715 | 21 | 334 | 1687[b] | (20) | 365 | 318 |
| | 1 | 20·0 | 3604 | 23 | 144 | 3304 | 252 | 34 | 5·28 | 1716 | 19 | 414 | — | — | — | 312 |
| VII | 2·0 | 9·93 | 3602 | 22 | 90 | 3176 | (298) | 80 | 9·93 | 1695 | (16) | (75) | 1675 | 15 | (275) | 775 |
| | 1·0 | — | — | — | — | | — | — | 9·93 | 1695 | (16) | (100) | 1675 | 14 | 312 | — |
| | 0·4 | 50·30 | 3605 | 26 | 140 | 3180 | — | (35) | — | — | — | — | — | — | — | 781 |
| VIII | 5·0 | 5·28 | 3591 | 23 | 55 | 3254 | 195 | 166 | 2·74 | 1677 | (19) | 165 | 1653 | 16 | 400 | 2145 |
| | 2·5 | 9·93 | 3592 | 22 | 75 | 3254 | 189 | 147 | 5·28 | 1673 | (17) | 185 | 1650 | 17 | 420 | 2174 |
| | 1·0 | 9·93 | 3592 | 23 | 110 | 3254 | 192 | 115 | 9·93 | 1674 | (16) | 240 | 1649 | 17 | 340 | 2138 |
| | 0·5 | 50·30 | 3593 | 22 | 125 | 3253 | 192 | 89 | — | — | — | — | — | | — | 2165 |

$\nu$ and $\Delta\nu_{\frac{1}{2}a}$ are in cm$^{-1}$. Values in parenthesis are approximate; sh—shoulder, K = [dimer/(monomer)$^2$]. In nujol $\nu$(OH); $\Delta\nu_{\frac{1}{2}a}$ (bonded): I 3319, (60), II 3416, (50), III 3246, (110), IV 3364, (210), V 3393, (44), VI 3394, (260), VII 3364, (82), VIII 3211, (150), [a] shoulder at 1680 cm$^{-1}$, [b] shoulder at 1675 cm$^{-1}$, —not measured.

## RESULTS AND DISCUSSION

From work to date,[3] it appears that self-association in phenols persists to an unusual extent only in cases where a ring of hydrogen bonds is spatially favoured. From IR data of the compounds investigated (Tables 1 and 2) self-association to very low concentrations is observed in those cases when phenolic compounds can adopt energetically favoured conformations and the hydrogen bonds are sterically protected against the solvent molecules.

Compounds I–III (Table 1) display two concentration-dependent bands in the OH and two in the CO regions in CCl$_4$. The presence of the bands assigned to the stretching vibrations of OH and CO groups bonded observed at milimolar concentration level suggest the dimeric association of a cyclic type, discussed previously,[3] is dominant. It follows from the association constants ($K$) of these compounds (Table 1), $K = [\text{dimer}/(\text{monomer})^2]$ in l mole$^{-1}$, calculated from the Mecke–Kempter equation,[5] that 3-hydroxy-4-methyl acetophenone (II) associates more strongly ($K \sim 370$ l mole$^{-1}$) than does ethyl 3-hydroxy-4-methyl benzoate I. This may be due to the fact that the rotation of the OR group in compound I weakens the H-bonding. The stronger self-association of 3-hydroxy-4-methyl acetophenone (II) than that observed with 3-hydroxy acetophenone[3] ($K \sim 120$ l mole$^{-1}$ in CCl$_4$) suggested that the introduction of the CH$_3$ group into *o*-position to the OH group the H-bonding is sterically protected against the solvent molecules. The lower association constant of 3-hydroxy-4-methyl benzonitrille (IV) ($K \sim 90$ l mole$^{-1}$) (Table 1) than that of 3-hydroxy-4-methyl-acetophenone (II) ($K \sim 370$ l mole$^{-1}$) or ethyl 3-hydroxy-4-methylbenzoate (I) ($K \sim 265$ l mole$^{-1}$) might be explained by the weak proton-acceptor nature of the CN group. It is interesting that the bonding shift in CCl$_4$, $\Delta\nu = \nu\text{OH(free)} - \nu\text{OH(bonded)}$ in compounds I–III is approximately the same ($\Delta\nu \sim 160$ cm$^{-1}$) whilst the association constant values differ markedly (Table 1).

TABLE 2. HYDROXYL AND CARBONYL ABSORPTIONS OF 3-HYDROXY-4-METHYL ACETOPHENONE (II) AND 2-HYDROXY-8-ACETYL NAPHTHALENE (VIII) IN CHCl$_3$

| Compound No. | Conc. (mM) | Cell paths (mm) | $\nu$(OH) | | | | | | Cell paths (mm) | $\nu$(CO) | | | K l/mole |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Free | | | Bonded | | | | | | | |
| | | | $\nu$ | $\Delta\nu_{\frac{1}{2}a}$ | $\varepsilon_a$ | $\nu$ | $\Delta\nu_{\frac{1}{2}a}$ | $\varepsilon_a$ | | $\nu$ | $\Delta\nu_{\frac{1}{2}a}$ | $\varepsilon_a$ | |
| II[a] | 100 | 0·474 | 3594 | 20 | 83 | 3405 | (150) | 90 | 0·1 | 1677 | 21 | 430 | 20 |
| | 50 | 0·474 | 3597 | 45 | 95 | 3406 | (180) | 70 | 0·2 | 1677 | 21 | 420 | 20 |
| | 25 | 0·964 | 3602 | 52 | 122 | 3406 | (190) | (58) | 0·474 | 1675 | 20 | 410 | 23 |
| VIII[b] | 50 | 0·474 | 3580 | 39 | 46 | 3248 | (238) | 139 | 0·2 | 1649 | (22) | 370 | 242 |
| | 40 | 0·474 | 3579 | 43 | 53 | 3250 | (242) | 134 | 0·474 | 1649 | (22) | 315 | 238 |
| | 25 | 0·964 | 3581 | 40 | 65 | 3250 | (236) | 123 | 0·964 | 1650 | — | 245 | 236 |
| | 10 | 2·736 | 3580 | (46) | 74 | 3254 | (230) | 100 | 2·736 | 1652 | — | 210 | 255 |

See for symbols Table 1;[a] overtone 2 $\nu$/CO at ~335 cm$^{-1}$;[b] the additional concentration dependent band at 1669 cm$^{-1}$, $\varepsilon_a$ of which increases with decreasing concentration (from 180 → 236 l mole$^{-1}$, cm$^{-1}$ over the range of concentrations studied).

In the case of compounds V and VI despite the number of possibilities for conformational freedom inherent in the molecules, the H-bonding is very strong (Table 1). The stereochemistry of these compounds must, therefore, be favourable to hydrogen bond formation (Fig 1) although the breadth of the absorption band $\nu(OH(bonded) \sim 3300\ cm^{-1}$ is much greater ($\Delta\nu_{\frac{1}{2}a} \sim 250\ cm^{-1}$) than that of compounds I–III. The high association constants (V, K $\sim$ 222 l $mole^{-1}$; VI, K $\sim$ 310 l $mole^{-1}$; (Table 1) indicate that the s-transoid conformation (Fig 1a) is preferable for the maintenance of conjugation in the system.

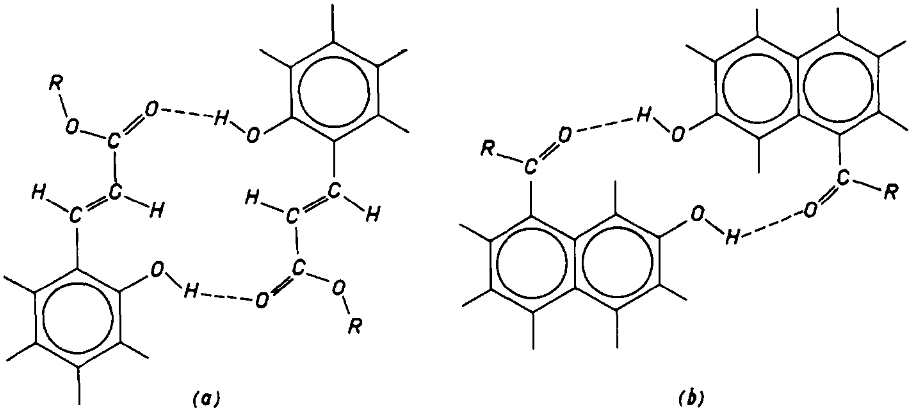
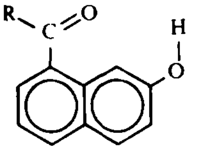


FIG 1. Planar projection of Dreiding models, a—VI and b—VIII. The dotted lines indicate the H-bonds.

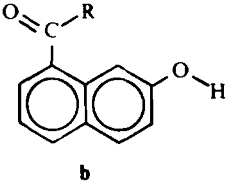
By comparing compounds V, VI (Table 1) and ethylcoumarate[3] it follows that the strength of association is appreciably weaker in compound V than that of n-propyl coumarate (VI) and ethylcoumarate[3] (K $\sim$ 420 l $mole^{-1}$). Similar values for the association constants of n-propyl coumarate VI and ethyl coumarate[3] suggest that the length of the alkyl chain attached to the oxygen of the carboxy group does not play any significant role. However, in the case of methyl coumarate (V), it seems that the H-bonding is less protected against the solvent molecules. Also the lowest association constant of methyl coumarate among the alkyl coumarates studied can probably be due to a conformation different from that adopted by the other coumarates studied.

The higher association constant of 2-hydroxy-benzalacetophenone (VII) as compared with that of compounds V and VI suggests that the situation in this compound is similar to that discussed with compounds I–III.

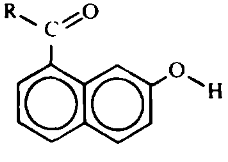
Of the compounds studied, the strongest association has been observed with 2-hydroxy-8-acetyl naphthalene (VIII) (K $\sim$ 2155 l $mole^{-1}$) (Table 1). The Dreiding molecular model (Fig 1b) shows that the interacting groups of two molecules of this compound are within bonding distance, that is the O···O distance is ~3 Å. Intramolecular H-bonding within a single molecule is not possible, as can be seen on the Dreiding model of this compound, due to a large distance between the functional groups and the stereochemistry (the O· · ·O distance is approximately ~ 4 Å) (Fig 1b). Of the four conformers (**a**, **b**, **c**, **d**) of compound VIII only two **a** and **c** would permit dimeric association by closure of the 16-membered ring through formation of twin H-bonds to the electron-rich carbonyl group



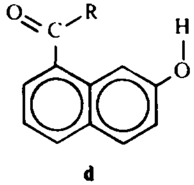
**a**



**b**



**c**



**d**

The intramolecular H-bonding in this compound is eliminated as confirmed by the presence of two concentration-dependent bands in the OH and CO regions (Table 1).

In conformers **b** and **d** the electrostatic repulsion of the $CH_3$ groups does not permit dimeric association. The strength of association is comparable with, but higher than that of alkylcoumarates V and VI. This can be explained by the fact that the number of possibilities for conformational freedom inherent in the molecule is lower than that with compounds V and VI. Also, the conjugated system, as with compounds V and VI and VII is, in compound VIII, extended by H-bonding.

The strength of association of compounds studied in $CHCl_3$ is reduced and some interaction with the solvent is to be expected (Table 2) e.g. broadening of the bands and decrease in wavenumber.

There is a marked change in the CO absorptions on passing from the $CCl_4$ to $CHCl_3$ solution and also the expected lowering in wavenumber by ~10 $cm^{-1}$ and the increase of the half-band width by 10 $cm^{-1}$ in compound II and by 23 $cm^{-1}$ and 5 $cm^{-1}$ in compound VIII, respectively. It is interesting that the self-association of

TABLE 3. UV ABSORPTION SPECTRAL DATA FOR 3-HYDROXY-4-METHYL ACETOPHENONE (II), 3-HYDROXY-4-METHYL BENZONITRILE (IV), n-PROPYL COUMARATE (VI) AND 2-HYDROXY-8-ACETYL NAPHTHALENE (VIII) IN CYCLOHEXANE

| Compound No. | Cell paths (cm) | Conc. (mM) | $\lambda_{max}$ (nm) | log $\varepsilon$ | $\lambda_{max}$ (nm) | log $\varepsilon$ | $\lambda_{max}$ (nm) | log $\varepsilon$ | $\lambda_{max}$ (nm) | log $\varepsilon$ |
|---|---|---|---|---|---|---|---|---|---|---|
| II | 1·0 | 0·25 | 306 | 3·43 | 299 | 3·46 | 273 | 3·28 | | |
| | 4·0 | 0·025 | 305 | 3·46 | 297 | 3·52 | 273 | 2·78 | | |
| IV | 1·0 | 0·20 | 294 | 3·61 | 284 | 3·59 | 240 | – | | |
| | 4·0 | 0·025 | 294 | 3·51 | 284 | 3·47 | 240 | 4·02 | | |
| VI | 0·1 | 1·0 | 325 | 3·91 | 318 | 3·95 | 307 | 3·87 | 273 | 4·26 |
| | 0·5 | 0·2 | 325 | 3·81 | 317 | 3·94 | 306 | 3·87 | 271 | 4·25 |
| | 1·0 | 0·1 | 325 | 3·79 | 315 | 3·93 | 306 | 3·84 | 270 | 4·25 |
| VIII | 1·0 | 0·25 | 350 | 3·66 | 309 | 3·57 | 297 | 3·50 | 271 | 4·08 |
| | 4·0 | 0·025 | 345 | 3·70 | 308 | 3·60 | 297 | 3·57 | 271 | 3·30 |

$\varepsilon$ in l $mole^{-1}$, $cm^{-1}$; —not measured.

compound VIII is so strong at the $10^{-2}$ M in $CHCl_3$ $\nu$OH(bonded); $\varepsilon_a$, 100 l mole$^{-1}$, cm$^{-1}$ and $\nu$OH(free); $\varepsilon_a$, 74 l mole$^{-1}$, cm$^{-1}$, although this solvent always solvates the more polar monomer.

The half-band width of bonded OH groups of compounds I, II, V and VII in nujol is relatively small (Table 1). This may indicate that these compounds exist only in the dimeric form with the two H-bonds in 14- or 16-membered rings, respectively.

The large half-band width of bonded OH groups with compounds VI and VIII $\Delta\nu_{\frac{1}{2}} \sim 260$ and 150 cm$^{-1}$, respectively, can be due to the overlapping of the bands with C–H aromatic bands in this region.

The UV data of the compounds studied (Table 3) show distinct molar absorptivity changes with concentration, e.g. with compound VIII, the band with $\lambda_{max} = 350$ nm, $\log \varepsilon = 3{\cdot}66$ is shifted to lower wave length ($\lambda_{max} = 345$ nm, $\log \varepsilon = 3{\cdot}70$) on passing from 0·25 to 0·025 mM in cyclohexane.

We have attempted, but with limited success, to support our conclusions from NMR spectroscopy. Anet and Muchowski[4] observed marked NMR shifts for changing concentrations of methyl-3-hydroxy-4-izopropyl benzoate the NMR of which was analysed as an ABX system. However, the solubility of compounds investigated, except for compound VI (Table 4) was too low for NMR analysis. In n-propyl coumarate (VI), it was possible to detect small but significant changes with concentration in the chemical shift values for the ethylenic protons (60 Mc/s spectrum, Table 4). In the concentration range (500 → 125 mM), the resonance signal of the OH proton in $CDCl_3$ was shifted from 2·53 to 3·57 $\tau$ and the same was observed for ethylenic protons ($H_a$ from 1·88 to 1·92 $\tau$ and $H_b$ from 3·32 to 3·35 $\tau$).

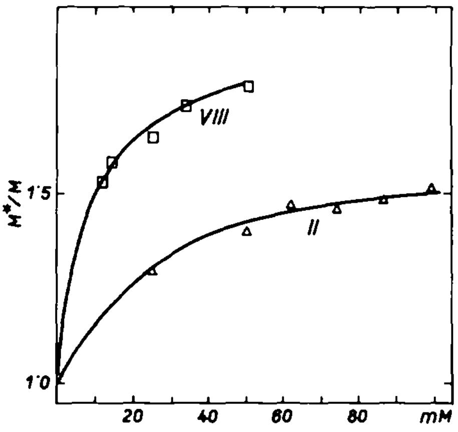
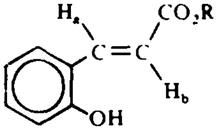


Fig 2. Plot of the ratio M*/M of the apparent M* to true M molecular weight against molar concentration for solutions in $CHCl_3$.

A plot of average molecular weight observed (M*) over true molecular weight (M) of the compounds II and VIII against molar concentration, determined by osmometry, reveals the dimeric association (Fig 2). All these results are in accord with the spectral data of these compounds.

TABLE 4. NMR DATA FOR METHYL COUMARATE (V) AND n-PROPYL COUMARATE (VI) (τ)

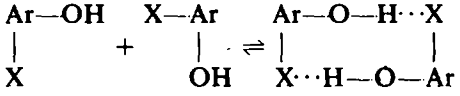


| Compound No. | Solvent | Conc. (mM) | $H_a$ | | $H_b$ | | OH |
|---|---|---|---|---|---|---|---|
| V | $CDCl_3$ | 75 | 1·81 | 2·08 | 3·24 | 3·51 | 3·76 |
| VI | $CDCl_3$ | 500 | 1·74 | 2·02 | 3·19 | 3·46 | 2·53 |
| | | 250 | 1·76 | 2·04 | 3·21 | 3·48 | 2·97 |
| | | 125 | 1·78 | 2·06 | 3·22 | 3·49 | 3·57 |
| | $CDCl_3 + D_2O$ | 500 | 1·75 | 2·02 | 3·22 | 3·50 | 5·37 |
| | | 250 | 1·77 | 2·04 | 3·23 | 3·51 | 5·38 |
| | | 125 | 1·79 | 2·07 | 3·23 | 3·52 | 5·38 |

V $J_{ab}$ 16·2 c/s; $—OCH_3$ 6·16, 2·3 → 3·3 τ (Ar—H).
VI $J_{ab}$ 16·8 c/s; $—O—CH_2—CH_2—CH_3$; Ar—H 2·3 → 3·3 τ
τ 5·78 8·26 9·01
J(c/s) 6·7 7·6 7·1

With compounds V, VI and VIII we have attempted to evaluate the H-bond enthalpies (—ΔH°) and entropies (—ΔS°). Assuming the dimer formation, the association constants were calculated according to the relation $K = [\text{dimer}/(\text{monomer})^2]$ in $1\ \text{mole}^{-1}$ at different temperatures.

For these systems the following equilibrium was assumed:



$$\begin{array}{c}\text{Ar—OH}\\|\\\text{X}\end{array} + \begin{array}{c}\text{X—Ar}\\|\\\text{OH}\end{array} \rightleftharpoons \begin{array}{ccc}\text{Ar—O—H}\cdots\text{X}\\|\qquad\qquad|\\\text{X}\cdots\text{H—O—Ar}\end{array}$$

The relatively constant values of the association constants over the range of concentrations studied suggest that the formation of cyclic "dimers" is dominant and the formation of "trimers" or "oligomers" can be neglected. This assumption seems to be reasonable because of their low concentrations (at milimolar level) at which the polymeric association is negligible. One may, therefore, conclude that the association constants calculated are reliable criteria for H-bonding in the systems studied.

For the determination of thermodynamic quantities of the systems studied the assumptions were made that the variation of cell thickness or the concentration with temperature is negligible over the range concerned.

The log $K$ values plotted against 1/T were found to fall on a straight line, from which the enthalpy (—ΔH°) and entropy (—ΔS°) changes for the hydrogen bond formation were obtained (Fig 3 and 4, Table 5). The results ensure the validity of the assumption of the equilibrium.

TABLE 5. THERMODYNAMIC QUANTITIES FOR COMPOUNDS V, VI AND VIII

| Compound No. | V | | | | | | VI | | | | | | VIII | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| °C | 25·2 | 30·5 | 34·5 | 40·5 | 45·0 | 52·5 | 25·5 | 33·2 | 37·6 | 43·0 | 47·3 | 52·5 | 21·5 | 30·5 | 36·0 | 38·8 | 47·2 | 52·0 |
| $\varepsilon_a$(OH) Bonded | 74 | 65 | 58 | 48 | 41 | 30 | 80 | 68 | 61 | 53 | 46 | 39 | 186 | 162 | 144 | 140 | 118 | 104 |
| $\varepsilon_a$(OH) Free | 92 | 100 | 105 | 113 | 119 | 128 | 90 | 100 | 106 | 112 | 118 | 124 | 48 | 59 | 68 | 68 | 84 | 93 |
| K(1 mole—$^1$) | 290 | 214 | 171 | 121 | 92 | 58 | 336 | 228 | 183 | 140 | 108 | 83 | 3777 | 2056 | 1320 | 1003 | 675 | 474 |
| ·ΔH° | 10·88 = 0·9 Kcal mole$^{-1}$ | | | | | | 9·48 = 0·9 Kcal mole$^{-1}$ | | | | | | 12·89 = 1·2 Kcal mole$^{-1}$ | | | | | |
| —ΔS° | 5·50 = 0·5 e.u. | | | | | | 4·40 = 0·5 e.u. | | | | | | 5·66 = 0·6 e.u. | | | | | |

All measurements were made in heated cells of 10 mm thickness in $CCl_4$; concentrations 5 mM.

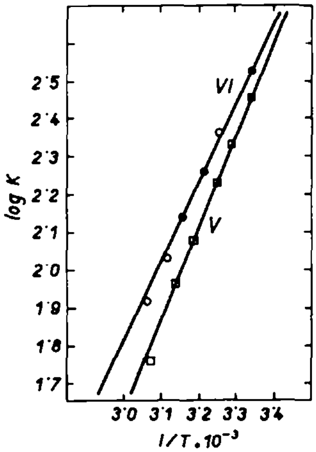


FIG 3. Plot of log $K$ against 1/T (V and VI in $CCl_4$).

From the plots of log $K$ against 1/T (Fig 3 and 4), $-\Delta H°$ and $-\Delta S°$ were determined by the relation

$$\log K = \frac{-\Delta H°}{R.T} + \frac{\Delta S°}{R}$$

The limits of accuracy were about $= 10\%$ for $-\Delta H°$ and $-\Delta S°$ (Table 5).

The high values of $-\Delta H°$ and $-\Delta S°$ for compounds V, VI and VIII demonstrate that the relation $-\Delta H° = 0{\cdot}016\ \Delta\nu(OH) + 0{\cdot}63$ suggested by Purcell and Drago[6] cannot be used in the present situation.

Compounds IX, X and XI show three bands in the 3100–3600 $cm^{-1}$ region assigned to the asymmetrical and symmetrical stretching vibration of the $NH_2$ groups free and bonded. However, the strength of association of these compounds was found to be small as compared with phenolic compounds studies.

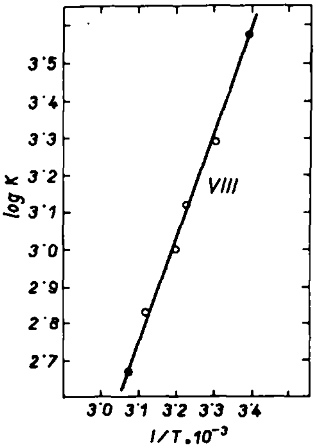


FIG 4. Plot of log $K$ against 1/T (VIII in $CCl_4$).

## EXPERIMENTAL

IR spectra were recorded with a Unicam S.P. 100 double beam instrument equipped with an S.P. 130 NaCl prism-grating double monochromator operated under the general procedure described previously.[3] Wavenumber measurements for the free and interbonded OH and CO 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, $\Delta\nu_{1/2}$ 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, $\varepsilon_a$(l $mole^{-1}$, $cm^{-1}$) rounded to the nearest integer and measured form a solvent–solvent base line. Association constants, $K$ = [dimer/(monomer)$^2$] in l $mole^{-1}$, were calculated from the Mecke–Kempter equation[5], $K = 1/ac(1 - \sqrt{a})$ where a is the value of the ratio of the apparent molar absorptivity of the OH band at concentration c (mole/1), to its value at infinite dilution. Although, the values of $K$ are approximate, they will serve as a guide to the degree of association. To obtain $-\Delta H°$ and $-\Delta S°$, the measurements were carried out at room temperature in 7·4 mm cells (concentration 5 mM in $CCl_4$) heated to 53°C. The temperature was measured by a calibrated thermometer inserted in the cell. Heating was by water from an ultrathermostat, and the temperature was accurate to ± 0·5°C. The thickness variation of the cells with temperature was neglected. The absorption cell was compensated by another fixed cell of the same thickness containing $CCl_4$.

UV spectra were recorded on a Perkin–Elmer, Model 450 double beam spectrophotometer in cyclohexane. NMR spectra were obtained with a Tesla BS-744 spectrometer (60 Mc/s) (TMS as internal standard) in $CDCl_3$. The mol wt measurements were made with a VPO Laboratorn´ prístroje, Czechoslovakia, vapour pressure osmometer precalibrated with benzil in $CHCl_3$ over a wide range of concentration in $CHCl_3$. Analar $CCl_4$ was used directly. Analar $CHCl_3$ was dried several times by passage through a column of blue silica gel before direct use. All compounds investigated were prepared according to the literature. Compounds V, VI and VII contained less than 1% of cis-isomer.

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