Hydrogen Bonding of Pyrrole, Indole and Carbazole with Substituted 1-Phenyl-2-pyrrolidinones

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We have recently reported the complex formation of substituted 1-phenyl-2-pyrrolidinones with iodine[1] and phenol.[2] In continuation of our efforts to elucidate the acceptor properties of these carboxamides, we are now investigating their association with NH proton donors. As indole has proved suitable for such studies,[3] we chose pyrrole, indole and carbazole for proton donors and measured by near infrared method the formation constants of their 1:1 complexes with eleven amides at four temperatures in carbon tetrachloride.

Experimental. 1-Methyl-2-pyrrolidinone and 1-phenyl-2-pyrrolidinones were available from our earlier studies.[1,2] Pyrrole, a *purum* product delivered by Fluka AG, Buchs, Switzerland, was distilled twice in the presence of barium oxide and preserved above molecular sieves. Indole was a reagent of analytical grade from E. Merck AG, Darmstadt, BRD, and used as received. Carbazole, a *purissimum* reagent from Fluka AG, was recrystallized from benzene. Carbon tetrachloride, a *Uvasol* reagent for spectroscopy from E. Merck AG, was dried and stored above Union Carbide Molecular Sieves Type 4A from British Drug Houses Ltd., Poole, England.

Spectrophotometric measurements were carried out and the values of the equilibrium constant K_{11} for the formation of the 1:1 complex were evaluated as described earlier.[2] The solutions were sufficiently dilute to prevent the self-association of the proton donors.[3,4] The self-association of 1-substituted 2-pyrrolidinones is not apparent. The values of the enthalpy of complexation $\Delta H°$ and the equilibrium constant K_{11}^{298} were determined from the plot of $\log K_{11}$ against $1/T$. These values were used for the calculation of $\Delta G°$ and $\Delta S°$. The spectra were recorded with a Beckman Model ACTA MIV spectrophotometer equipped with a specially designed thermostated cell holder.

Results and discussion. The values of K_{11}^{298}, $\Delta H°$, $\Delta G°$ and $\Delta S°$ and the values of $\Delta\nu_{NH}$, the wave number difference between the free and associated NH-groups are given in Table 1.

The value of $\log K_{11}^{298}$ for unsubstituted and seven *p*- and *m*-substituted compounds, when plotted against Hammett σ-values,[5] yielded for pyrrole the equation

$$\log K_{11}^{298} = (-0.64 \pm 0.09)\sigma + (0.75 \pm 0.02) \tag{1}$$

with a correlation coefficient of 0.942, for indole the equation

$$\log K_{11}^{298} = (-0.54 \pm 0.05)\sigma + (1.00 \pm 0.01) \tag{2}$$

with a correlation coefficient of 0.977, and for carbazole the equation

$$\log K_{11}^{298} = (-0.60 \pm 0.08)\sigma + (1.11 \pm 0.02) \tag{3}$$

with a correlation coefficient of 0.955.

If the values of the wave number shift $\Delta\nu_{NH}$ are expressed as a function of Hammett σ-values, they yield for pyrrole the equation

$$\Delta\nu_{NH} = (-31.2 \pm 2.9)\sigma + (129 \pm 1) \tag{4}$$

with a correlation coefficient of 0.977, for indole the equation

$$\Delta\nu_{NH} = (-36.5 \pm 3.5)\sigma + (140 \pm 1) \tag{5}$$

with a correlation coefficient of 0.974, and for carbazole the equation

$$\Delta\nu_{NH} = (-34.2 \pm 4.2)\sigma + (143 \pm 1) \tag{6}$$

with a correlation coefficient of 0.957.

Comparison of the values of K_{11}^{298}, $\Delta H°$ and $\Delta\nu_{NH}$ shows 1-methyl-2-pyrrolidinone to be a stronger hydrogen-bond acceptor than the *p*- and *m*-substituted 1-phenyl-2-pyrrolidinones, and this holds good for both the number and strength of the bonds. The same observation was made earlier when we studied the complexation of the same compounds with phenol and iodine; the stronger acceptor properties of 1-methyl-2-pyrrolidinone have been attributed to the increased resonance contribution of the carboxamide group.[1,2]

The values of K_{11}^{298} for the complexation of pyrrole, indole and carbazole with 1-phenyl-2-pyrrolidinone are 6.30, 10.1 and 13.9 dm^3 mol^{-1}, respectively. This sequence is the same as found when they form complexes with triethyl- and triphenylphosphine oxides.[6] The sequence parallels that of increasing acid strength of the proton donors, as revealed by the increased number of resonance forms of the corresponding anions. The value 17.51 has been measured for pK_a of pyrrole and 16.97 for indole.[7] The N−H stretching frequencies are 3496, 3491 and 3485 cm^{-1} for pyrrole, indole and carbazole, respectively.[8]

The pK_a value of phenol in water is about seven pK units lower than that of indole. The difference between the hydrogen-bond complexation constants is much smaller, as K_{11}^{298} for the phenol-1-

Table 1. Hydrogen bonding data for complexes of pyrrole, indole and carbazole with various 2-pyrrolidinones in carbon tetrachloride at 25 °C.

1-Substituent in 2-pyrrolidinone	K_{11}^{298} $dm^3 mol^{-1}$	$-\Delta G°$ $kJ mol^{-1}$	$-\Delta H°$ $kJ mol^{-1}$	$-\Delta S°$ $J K^{-1} mol^{-1}$	$\Delta\nu_{NH}$ cm^{-1}
Pyrrole					
4'-Methoxyphenyl	8.24	5.228	11.0	19.5	138
4'-Methylphenyl	6.61	4.681	11.9	24.1	133
4'-Ethylphenyl	6.95	4.806	11.3	21.6	133
3'-Methylphenyl	6.37	4.590	11.3	22.4	131
Phenyl	6.30	4.562	11.6	23.7	131
3'-Methoxyphenyl	5.92	4.408	10.9	21.7	128
4'-Chlorophenyl	3.52	3.119	9.71	22.1	122
3'-Chlorophenyl	3.12	2.820	8.85	20.2	116
2'-Methylphenyl	13.0	6.358	15.3	30.0	157
2'-Chlorophenyl	9.58	5.601	12.4	22.8	142
Methyl	15.7	6.826	13.0	20.7	161
Indole					
4'-Methoxyphenyl	13.6	6.470	14.0	25.1	152
4'-Methylphenyl	12.5	6.261	13.8	25.1	146
4'-Ethylphenyl	12.7	6.300	13.1	22.9	146
3'-Methylphenyl	10.7	5.875	13.3	25.0	140
Phenyl	10.1	5.732	13.6	26.5	143
3'-Methoxyphenyl	9.59	5.604	11.6	20.0	134
4'-Chlorophenyl	6.84	4.766	10.6	19.7	132
3'-Chlorophenyl	6.51	4.644	12.1	25.1	128
2'-Methylphenyl	20.9	7.535	15.9	28.1	168
2'-Chlorophenyl	18.0	7.165	14.6	24.9	156
Methyl	34.4	8.770	14.7	20.0	181
Carbazole					
4'-Methoxyphenyl	18.6	7.246	14.4	23.9	156
4'-Methylphenyl	15.0	6.713	13.0	21.0	148
4'-Ethylphenyl	15.6	6.810	13.4	22.1	147
3'-Methylphenyl	14.3	6.594	13.0	21.5	144
Phenyl	13.9	6.524	11.9	17.9	140
3'-Methoxyphenyl	12.9	6.339	12.8	21.8	141
4'-Chlorophenyl	8.17	5.207	12.4	24.1	134
3'-Chlorophenyl	7.66	5.047	11.6	22.0	132
2'-Methylphenyl	27.9	8.251	14.6	21.2	163
2'-Chlorophenyl	23.9	7.867	13.9	20.4	155
Methyl	30.6	8.480	13.8	17.8	184

phenyl-2-pyrrolidinone system is 41.3 dm³ mol⁻¹.[2] The hydrogen bonds have been studied in carbon tetrachloride, *i.e.* in a solvent of much lower polarity, where the relative acidities of the proton donors might be closer to each other, however. It is well-known that, compared with hydroxylic solvents, aprotic solvents exert a levelling effect on the nucleophilic reactivities of different anions.[9]

The values of $\Delta H°$ in the table support the conclusion that the hydrogen bond is also stronger

the higher the value of K_{11}^{298}.

The value of the reaction constant of the Hammett equation is -0.594 when substituted 1-phenyl-2-pyrrolidinones form complexes with phenol[2] and -0.519 when they form complexes with iodine.[1] These values do not differ much from those found in this study, indicating approximately the same change of electron density in the complexations regardless of the other participant. This phenomenon does not hold when substituted phenols

form hydrogen bonds to 1-methyl-2-pyrrolidinone and other amides.[10] Moreover, when substituted phenols form complexes with several oxygen proton acceptors, the reaction constant is linearly correlated with the complexation enthalpy.[10] This last correlation in turn does not exist for substituted 1-phenyl-2-pyrrolidinones.

2′-Methyl and 2′-chloro substituents increase the values of K_{11}^{298}, $\Delta H°$ and $\Delta \nu_{NH}$. This can be explained by polar substituent effects. The chloro substituent produces on the 1′-carbon atom a partial negative charge which stabilizes electrostatically the positive charge on the 1-nitrogen atom of 2-pyrrolidinone. Superimposed on the $+I$-effect, the methyl substituent effect works in the same way, but the resonance arises from the Baker-Nathan effect.

The values of $\Delta \nu$ are clearly larger when 1-phenyl-2-pyrrolidinones form complexes with phenol. Remembering the similar values of the reaction constant, it is of interest that the values of the slopes fall in the same region for all proton donors, $\Delta \nu_{OH} = -36.7\sigma + 318$ for phenol.[2]

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