

Short note

Studies on hydrogen bonded complexes
Proton transfer equilibria and thermodynamic parameters of hydrogen
bonded complexes in 2,4-dinitro-1-naphthol–amine systemsMoustafa M. Habib^a, Ezzat A. Hamed^{b,*}, Aziza K. Shehata^a,
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The formation of hydrogen bonded complexes between 2,4-dinitro-1-naphthol (DNN) and various nitrogen bases was investigated by UV spectroscopy in benzene. The interaction between DNN and the aromatic tertiary amine, *N*-methylimidazole (NMI), led to 1:1 complex formation at lower concentrations of NMI. A characteristic absorption band appeared at 418 nm and an isosbestic point at 352 nm. At higher concentrations of NMI, the spectra showed a band at 440 nm, which is presumably attributable to a proton detachment from the phenol molecule as a result of formation of a homo-conjugated cation $[N \cdots H \cdots N]^+$. In this case, we are dealing with the free naphthoxide anion.

The UV spectra of hydrogen bonding interaction between DNN and the secondary amines, i.e. morpholine (Mo), piperidine (Pip), and diethylamine (DEA) were analyzed. Using Mo, two bands appeared at 412 and 417 nm, and two isosbestic points at 346 and 466 nm at low and high concentrations of Mo, suggesting the formation of 1:1 and 1:2 complexes, respectively. The same behaviour was found in the case of Pip, where two bands at 411 and 415 nm, and two isosbestic points at 346 and 458 nm were observed. The maximum absorption of the free naphthoxide ion lies at lower wavelengths: 417 nm in the case of Mo and 415 nm in the case of Pip, compared with the observed 440 nm maximum absorption assigned to NMI. This is due to the interaction between the naphthoxide ion and the amine through the hydrogen bond, which stabilizes the ground state of the anion. This shifts the band in question towards lower wavelength. In the case of DEA, its maximum absorption of the naphthoxide ion appeared at 433 nm, where the ground state is destabilized, and shifts the absorption band towards a higher wavelength compared with that for Mo and Pip.

The UV spectra of triethylamine (TEA) and *n*-pentylamine (*n*-PA) with DNN revealed one isosbestic point at 350 and 462 nm respectively, suggesting 1:1 complex formation. In such compounds, no free anion is formed, as they are not capable of forming the homo-conjugated cation due to steric hindrance effect.

The equilibrium constants K_{eq} of 1:1 proton transfer (PT) complex formation were calculated using the Rose–Drago and the minimum–maximum methods. The plot of $\log K_{eq}$ versus the aqueous pK_a of the amines showed a linear correlation, except for those compounds exhibiting steric hindrance. The thermodynamic parameters were determined; the values of ΔH° were in the range of -12 to -26 kcal mol⁻¹ and those of ΔG° in the range of -2.89 to -4.46 kcal mol⁻¹, suggesting a strong OHN hydrogen bonding bridge.

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The PT process is controlled rather by entropy than by enthalpy. The higher negative value of ΔS° for TEA, $-69.74 \text{ cal K}^{-1}$, is attributed to the formation of an amine-solvated PT complex, where the DNN and the sterically hindered TEA molecules are involved. The least negative value for *n*-PA, $-31.84 \text{ cal K}^{-1}$, corroborates the suggestion of 1:1 complex formation. The relatively higher value of ΔS° in the case of the DEA system $-41.30 \text{ cal K}^{-1}$, is due to the summation of entropies of different hydrogen bonded species existing in equilibrium.

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