at the sidechain is found to occur at 7·2 ppm while the benzyllic protons appear at 6·3 ppm; the phenyl ring protons can be seen at about 3 ppm, close to the peak due to the proton impurity in CDCl₃.

As the DCA concentration in the mixture increases, all the peaks of PSBC are found to get sharper until about 25% DCA, when the spectrum is indistinguishable from that in pure DCA. Concurrent with the reduction in the linewidths of the peaks, one also observes a chemical shift of the peaks towards the downfield region (with respect to TMS).

The observed changes in the spectra with increasing DCA concentration can be interpreted as a conformational transition from a relatively highly ordered to a disordered state of the polypeptide on the basis of: (a) the relatively broad peaks in 98% CDCl₃ as contrasted with the sharper ones in pure DCA indicating more mobility of the respective protons and (b) the downfield chemical shift of the peaks which is found to occur in the helix-coil transition in polypeptides. That this transition could represent a β-structure → coil transition is derived from the facts that (a) in compounds similar in structure to PSBC, such a transition in CDCl₃-DCA mixture has been reported and (b) the ORD studies of Fraser et al. on PSBC in ethylenedichloride-DCA mixture indicate the possibility of a β → coil transition.

Further studies using ORD and UV spectral measurements to confirm our conjecture are being carried out and will be presented elsewhere.

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Molecular Biophysics V. S. ANANTHANARAYANAN
Unit, K. R. K. EASWARAN
Indian Institute of Sci., Bangalore-560012.
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CRYSTAL DATA ON MONOBROMOMOHYPHALANTHIN
As a part of a programme of studying the structures of physiologically active compounds in this laboratory, the authors have taken up the structure of Monobromohypallanthin (C₂₄H₂₅O₇Br). Figure 1 shows the structural formula of Monobromohypallanthin as given by L. R. Row and P. Satyanarayana. The composition was determined by elemental chemical analysis (C, H, O, Br). This communication presents the crystal data of the substance.

![Crystal structure](image)

The substance supplied by Prof. Ramachandra Row of the Andhra University, is crystallized by solution in methyl alcohol. The unit cell dimensions and space group of the crystal are determined from oscillation and Weissenberg photographs. The density of the crystal is determined by floatation in zinc chloride solution.

An examination of the Weissenberg photographs shows the following systematic absences only.

h 00, h odd; O KO, K odd and OO 1, 1 odd.

This uniquely determines the space group of the crystal as P₂₁₂₁. The crystal data are as follows:

**Crystal data**

- Chemical formula: C₂₄H₂₅O₇Br
- Molecular weight: 569·37
- Dimensions: a = 28·80 ± 0·02 Å, b = 13·46 ± 0·01 Å, c = 6·06 ± 0·01 Å
- Cell volume: 2349·15 Å³
- Density calculated, D = 1·438 gm cm⁻³
- Density experimental, D = 1·430 gm cm⁻³
- Number of molecules in the unit cell: 4
- Crystal system: Orthorhombic
- Space group: P₂₁₂₁
- μ for Cu Kα: 29·93 cm⁻¹
Further study on the crystal is in progress.

The authors wish to thank Prof. K. V. Krishna Rao, for his keen interest and Prof. L. Ramachandra Row, for providing them with substance. Our thanks are also due to the National Bureau of Standards, U.S.A., for financing a Research Scheme under which this work is done.

Physics Department, SVED BURJAHULLAH QADRI,
Osmania University, B. RAM PRASAD,
Hyderabad-500007, India,
February 26, 1974.


PROTON-LIGAND STABILITY CONSTANTS OF SUBSTITUTED NAPHTHOLS IN 50% V/V ACETONE-WATER MIXTURE

The presence of substituents at different positions in an organic molecule affects the pK value of its dissociable protons. The effects are generally additive and in most cases they are due to inductive, resonance and steric effects. A number of empirical relations have been proposed in the past so that the prediction of an acid (or base) strength of an organic compound can be made with reasonable accuracy. Since pK values are required for the determination of metal ligand stability constants, we present in this paper the proton-ligand stability constants of 1-naphthol and some of the substituted naphthols. The proton-ligand stability constants were determined by potentiometric method using Bjerrum's method as modified by Chaberek and Martell.

Material and Methods.—1-naphthol, 1-hydroxy-naphthalene 4-sulphonic acid (Na-Salt), 1-hydroxy 2-naphthoic acid and nitroso-R-Salt were obtained from Fluka Company. 2-nitroso 1-naphthol and 1-amino 2-hydroxynaphthalene 4-sulphonic acid were of B.D.H. quality. 1-Hydroxy 2-nitrosonaphthalene 4-sulphonic acid and 2-acetyl 1-naphthol were prepared by the reported literature methods. Appropriate quantities of the reagents were dissolved in double distilled water and titrated potentiometrically. The acetone was of A.R. grade.

An ELICO pH Meter Model LI-10 with ELICO glass and Calomel electrodes capable of reading ±0.02 was employed for the pH measurements. The pH meter was standardised with buffers of pH 4.00 and 9.00.

The pH titrations of the acids were conducted in a double wall jacketed glass cell through which water from a thermostat was circulated. The temperature within the cell containing dilute solution of the acid of known concentration (Ca., 2 × 10⁻³ M) was maintained within ±0.1°C. Once the solution attained the required temperature it was titrated by the addition of small amounts of standard alkali from a calibrated 5 ml microburette at a time and noting the pH. The ionic strength was kept constant by using a medium of 0.1 M KNO₃. Solutions of 1-hydroxy 2-naphthoic acid, 1-naphthol, 2-acetyl 1-naphthol, 1-hydroxy-naphthalene 4-sulphonic acid, 2-nitroso 1-naphthol, nitroso-R-Salt and 1-hydroxy 2-nitrosonaphthalene 4-sulphonic acid were prepared in 50% V/V acetone-water mixture using distilled water free from carbon dioxide. The pH values were corrected in all aquo-organic mixtures using the method of Van Uitert and Haas.

Results and Discussion.—The proton-ligand stability constant of hydroxyl group of 1-naphthol and other substituted naphthols in 50% V/V acetone-water mixture at a constant ionic strength of 0.1 M KNO₃ and 35°C are presented in Table I. The pK values of phenolic proton are in the following order.

1-Hydroxy 2-naphthoic acid > 1-naphthol > 2-acetyl 1-naphthol > 1-hydroxynaphthalene 4-sulphonic acid > 1-amino 2-hydroxy naphthalene 4-sulphonic acid > 2-nitroso 1-naphthol > nitroso-R-Salt > 1-hydroxy 2-nitroso naphthalene 4-sulphonic acid.

The introduction of electron withdrawing groups like nitroso, acetyl in ortho position and sulphonic in para position favours the easy liberation of phenolic proton in solution. As a result the pK value decreases in comparison with 1-naphthol. The higher value of 1-hydroxy 2-naphthoic acid is ascribed to intramolecular hydrogen bonding similar to salicylic acid. The low pK value of 2-nitroso 1-naphthol in comparison with 1-hydroxy 4-sulphonic acid is due to the fall in inductive effect from ortho to para position.

In the case of 1-hydroxy 2-nitrosonaphthalene 4-sulphonic acid, the effects are additive due to the substitution in 2 and 4 positions. The predicted pK value is calculated as shown below:

decrease in pK for the substitution of nitroso group at 2-position = 10.96 - 8.16 = 2.80,
decrease in pK for the substitution of sulphonic acid in 4-position = 10.96 - 9.81 = 1.15,
extected decrease in pK for the substitution of nitroso at 2-position and sulphonic acid group at 4-position = 2.80 + 1.15 = 3.95.