TABLE III

*Mean amplitude of vibration (in $10^{-2} \times$ Å) of some bent XYZ molecules*

| Symbol | HOF | | | DOF | | |
|---|---|---|---|---|---|---|
| | T = 0° K | T = 298° K | T = 500° K | T = 0° K | T = 298° K | T = 500° K |
| $U_{x-y}$ .. | 7·049 | 7·049 | 7·049 | 5·964 | 5·964 | 5·964 |
| $U_{x-z}$ .. | 3·783 | 3·796 | 3·882 | 4·610 | 4·694 | 4·834 |
| $U_{y---z}$ .. | 14·387 | 14·707 | 15·701 | 12·774 | 12·791 | 12·810 |

for both bonded and non-bonded distances increases with the increase in the temperature.

Department of Physics,
University of Gorakhpur,
Gorakhpur-273001,
*January* 29, 1974.

NITISH K. SANYAL.
A. K. GANGULI.
L. DIXIT.

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## NMR STUDIES ON POLY (S-BENZYL-L-CYSTEINE) IN SOLUTION

IN a recent review by one of us[1] the need for a systematic study of the $\beta$-structure in polypeptides by various physical techniques was emphasized. As part of our studies in this direction, we report in this communication our results on the nuclear magnetic resonance (NMR) studies on poly (S-benzyl-L-cysteine) [PSBC] in mixtures of deuterated chloroform ($CDCl_3$) and dichloroacetic acid (DCA). The results indicate that a conformational change occurs in the polypeptide in going from $CDCl_3$ to DCA solution ; this change is likely to be a $\beta$-structure $\rightarrow$ coil transition.

PSBC was obtained from Sigma Chemical Co., U.S.A. (M.wt. $\simeq$ 5000). DCA from Riedel was distilled under vacuum before use. $CDCl_3$ was from Stohler Chemicals, U.S.A., containing 99% deuterated form. The NMR spectra were taken at 100 Mc/sec on the HA-100 NMR spectrometer of Varian, Inc., U.S.A. The samples were maintained at 31°. Tetramethylsilane (TMS) from Stohler Chemicals, U.S.A., was used as the reference compound except when pure DCA was used as the solvent ; in the latter case, the lock was made on the CH-proton signal of DCA.

Figure 1 shows the NMR spectra of PSBC as a function of $CDCl_3$-DCA mixture composition. The bottom-most spectrum was obtained by weighing approximately 10 to 12 mg of the sample in the NMR sample tube, adding 0·01 ml of DCA to wet the sample and then 0·5 ml $CDCl_3$ and mixing the contents. The other spectra were obtained by successively adding the required quantity of DCA to the solution and mixing. The top-most spectrum was obtained by dissolving the substance in pure DCA.

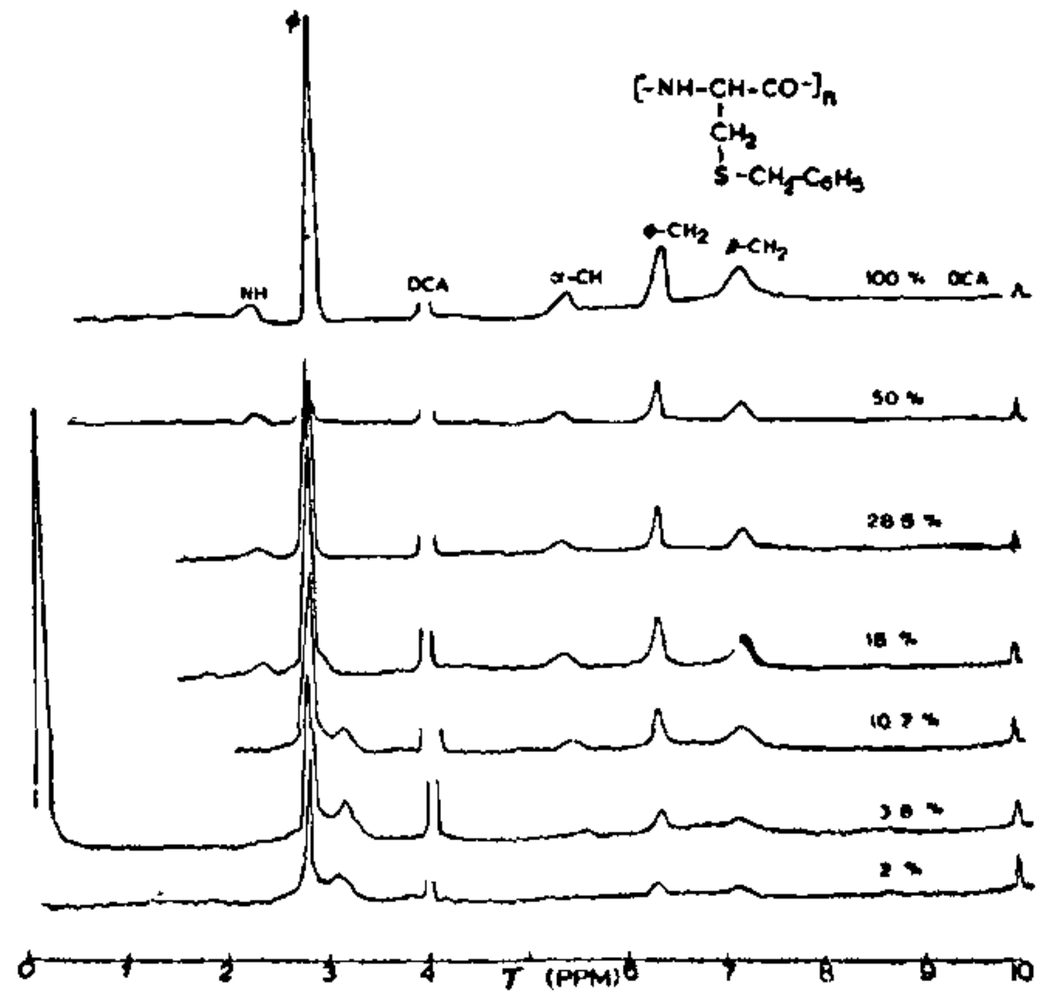


FIG. 1. Proton NMR spectra of PSBC at various $CDCl_3$-DCA mixtures. The internal reference is TMS.

The spectrum in 98% (v/v) $CDCl_3$ solution is seen to consist of relatively broad peaks which can be assigned to the various protons as indicated in the figure. These assignments were made on the basis of available knowledge of NMR of polypeptides[3]. The peak due to the NH proton of the polypeptide backbone occurs at about 2·3 ppm and that of the α-CH proton at about 5·6 ppm and are only barely visible at this composition of the solvent mixture. The peaks due to the $\beta$-$CH_2$ protons

at the sidechain is found to occur at 7·2 ppm while the benzylic 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 $CDCl_3$.

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% $CDCl_3$ 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[3] That this transition could represent a $\beta$-structure $\rightarrow$ coil transition is derived from the facts that (*a*) in compounds similar in structure to PSBC, such a transition in $CDCl_3$—DCA mixture has been reported[2] and (*b*) the ORD studies of Fraser *et al.*[4] on PSBC in ethylenedichloride-DCA mixture indicate the possibility of a $\beta \rightarrow$ coil transition.

Further studies using ORD and UV spectral measurements to confirm our conjecture are being carried out and will be presented elsewhere[5].

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Molecular Biophysics Unit,
Indian Institute of Sci.,
Bangalore-560012,
*January* 17, 1974.

V. S. ANANTHANARAYANAN.
K. R. K. EASWARAN.

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## CRYSTAL DATA ON MONOBROMO-HYPOPHYLLANTHIN

As a part of a programme[1-2] of studying the structures of physiologically active compounds in this laboratory, the authors have taken up the structure of Monobromohypophyllanthin ($C_{24}H_{29}O_7Br$). Figure 1 shows the structural formula of Monobromohypophyllanthin as given by L. R. Row and P. Satyanarayana. The composition[3] was determined by elemental chemical analysis (C, H, O, Br). This communication presents the crystal data of the substance.

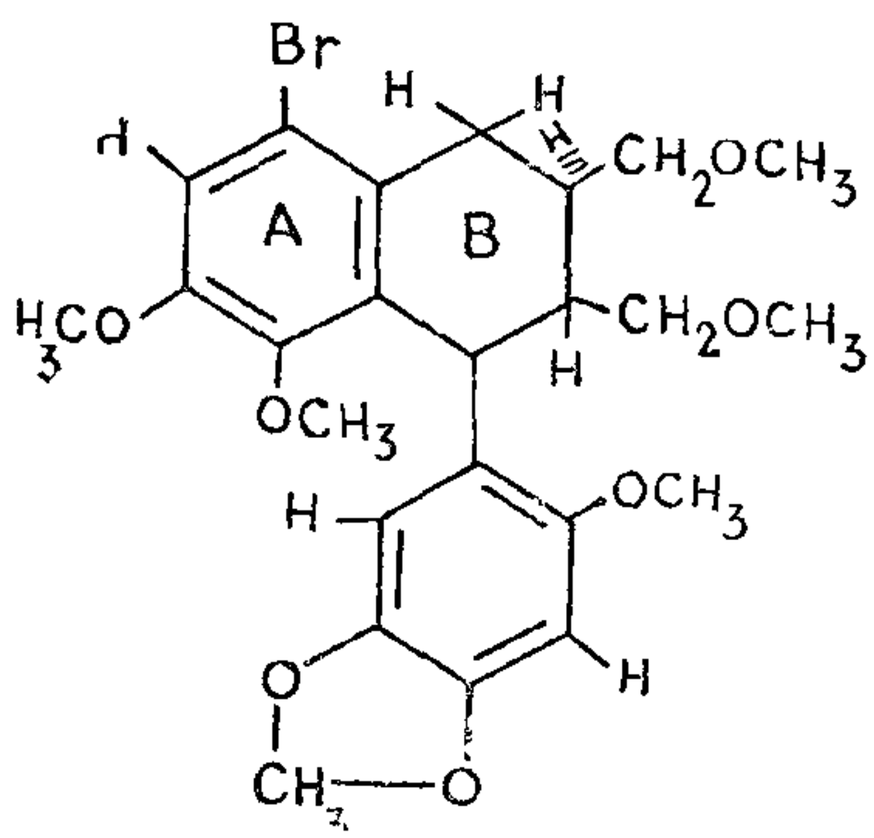


FIG. 1

The substance supplied by Prof. Ramachandra Row of the Andhra University, is crystallised 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* OO, *h* odd; O KO, K odd and OO 1, 1 odd.

This uniquely determines the space group of the crystal as $P_{2_12_12_1}$. The crystal data are as follows:

| Crystal data | | |
|---|---|---|
| Chemical formula | | $C_{24}H_{29}O_7Br$ |
| Molecular weight | | 509·37 |
| *a* | = | 28·80 ± 0·02 Å |
| *b* | = | 13·46 ± 0·01 Å |
| *c* | = | 6·06 ± 0·01 Å |
| Cell volume | = | 2349·15 Å$^3$ |
| Density calculated, $D_c$ | = | 1·438 gm cm$^{-3}$ |
| Density experimental, $D_e$ | = | 1·430 gm cm$^{-3}$ |
| Number of molecules in the unit cell | = | 4 |
| Crystal system | | Orthorhombic |
| Space group | | $P_{2_12_12_1}$ |
| $\mu$ for Cu $K_\alpha$ | | 29·93 cm$^{-1}$ |