

SYNTHESIS CHARACTERISATION AND ¹H-NMR STUDIES OF SOME BIS POLYMERIC LIGANDS

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ABSTRACT

Different ligands of p-bromophenyl urea with adipic acid, azelaic acid, succinic acid, sebacic acid and subaric acid have been prepared in benzene medium by condensation process. The structural composition has been determined from elemental analysis, ¹H-NMR and IR spectra. The spectral assignment of NMR has been done with the help of distortion less enhancement by polarization transfer and the H-H coupling are explained with the help of total correlated spectroscopy.

Key words: ¹H-NMR studies, bis polymeric ligand and p-bromo phenyl urea.

INTRODUCTION

¹H-NMR Spectroscopy is a powerful technique for investigating nuclear structure of any organic compounds. Now a days proton NMR technique can be used for determination of stereochemical structure and conformational analysis of polymer compounds^{1,2}. The chemical shift in NMR spectrum, indicates that what type of hydrogen atoms are present e.g. methylene, methyl groups, olefins, ethers, esters and aromatic compounds^{3,4}. 2D-NMR methods have been used as a powerful and reliable techniques for determination of compositional and configurationally structure of co-ordination polymer. Polyvinyl pyridine and its copolymers have important applications as polyelectrolyte, polymer reagents and in electrical applications⁵.

A literature survey however reveals that ligands of p-bromophenyl urea with adipic acid, azelaic acid, succinic acid, sebacic acid and subaric acid which can be used for the preparation of chelate polymers of first transition metal ions. These ligands have been synthesized in our laboratories and characterized by various instrumental techniques.

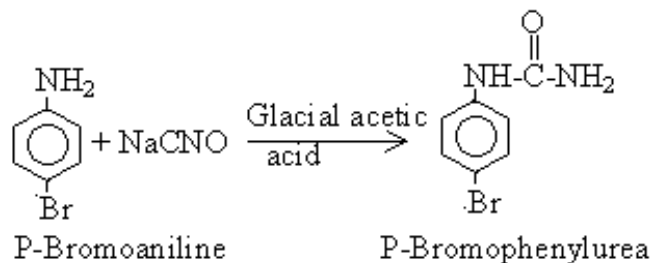
EXPERIMENTAL

Chemicals: Analytical Reagent Grade Chemicals were used.

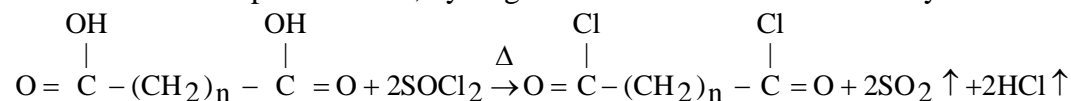
Instruments: C, H, N element contents were analysed on E. A. 1108 Carlo Erba Instrument. ¹H-NMR (CDCl₃, DMSO-d₆) spectra were recorded on Bruker model DRX-30 NMR Spectrophotometer using TMS as internal reference (δ ppm). FTIR spectra were recorded on Nicolet magna IR 550 series2, spectrophotometer, USA, using KBr Technique in the wavelength 400-4000 cm⁻¹ at Regional Sophisticated Instrumentation Centre, Lucknow. Bromine contents were analysed at National Chemical Laboratory, Pune.

Preparation of p-bromo phenyl urea ⁶: A quantity of 17.10 gm (0.1 m mol) of finely powdered p-bromo aniline was dissolved in a mixture of 100 ml glacial acetic acid and 200 ml distilled

water at 35°C. Then 6.5 gm (0.1 m mol) sodium cyanate in 100 ml distilled water at 35°C added gradually with constant stirring. Solid product obtained was filtered and recrystallized from 90% aqueous ethanol.



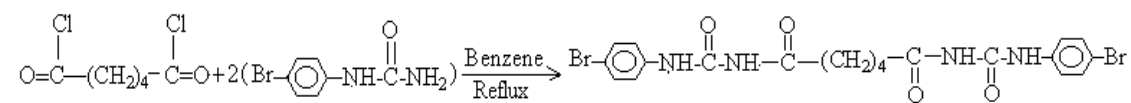
Preparation of dichloride of adipic, azelaic, succinic, sebacic and subaric acid: A quantity of (0.1m mol) dry acid and (0.25m mol) double distilled thionyl chloride was taken in 100ml dry round-bottomed flask fitted with water condenser provided with guard tube containing unhydrous calcium chloride. Flask was heated on a water bath for about 2-3 hours, till clear solution was obtained. The reaction mixture was then refluxed under reduced pressure for 30 min. to remove sulphur dioxide, hydrogen chloride and unreacted thionyl chloride.



(1) n=4 for adipic acid (2) n=7 for azelaic acid (3) n=2 for succinic acid (4) n=8 for sebacic acid (5) n=6 for subaric acid.

Preparation of ligand:

The ligand adipyl bis-p-bromophenyl urea was prepared by the condensation of acid dichloride (0.1m mol) with p-bromophenyl urea (0.2m mol) in sodium-dried benzene for about 4-5 hours. The ligand was filtered and washed with hot ethanol to remove unreacted p-bromophenyl urea and dried in oven at 100°C then it was characterised by elemental analyses and infrared spectra.



RESULTS AND DISCUSSION

The ¹H-NMR Spectrum of p-bromo phenyl urea with adipic acid, azelaic acid, succinic acid, sebacic acid and subaric acid in acetone solvent along with complete assignments of resonances signals for aliphatic and aromatic protons are shown in Figs.1 to 5.

The NMR signal around δ(chemical shift) 2.05-2.40 ppm is assigned to the over laps of -CH₂-protons of Ligands⁷. The aromatic protons of two phenyl groups are appeared at δ 7.48-7.63 ppm due to the presence of(-NHC=O) amide groups attached directly to benzene ring⁸ and other resonance signal around δ 7.35-7.47 ppm is assigned due to two protons of benzene ring at which bromine attached^{9,10}.

The resonance weak signal around δ 4.54-5.64 ppm is assigned to -NH-region of ligands and other weak signal around δ 8.24-8.27 ppm is assigned two protons of amide group (-NHC=O)¹¹. In the infrared spectrum of the ligands a weak bands appeared from 3427-3480 cm^{-1} due to the presence of stretching vibration of the NH group¹². Another sharp bands observed from 1606-1700 cm^{-1} may be assigned due to the C=O stretching vibrations¹³. A weak band appeared from 2882-2940 cm^{-1} may be assigned due to stretching vibrations of -CH₂- groups¹⁴. ¹H-NMR, elemental analyses and infra-red spectra assignment of ligands are shown in Table 1, 2 and 3.

Table-1: ¹H-NMR Spectral Data of Ligands

Observed Chemical Shift (δ) ppm					Nature of proton assigned	Expt. Chemical Shift (δ) ppm
ADBPBU	AZPBPU	SAPBPU	SBPBPU	SUPBPU		
2.03 – 2.38	2.03 – 2.31	2.08 – 3.30	2.03 – 2.32	2.03 – 2.40	Methylene proton of -CO-(CH ₂) _n -CO	1.4 – 2.4
4.54	5.58	5.60	5.58	5.64	Proton of Nitrogen of -C-NH-CO-	5.16
7.35 – 7.47	7.34 – 7.44	7.34 – 7.47	7.41 – 7.45	7.35 -7.44	Aromatic Proton of Ar-H	7.41

Table-2: Elemental Analyses of Ligands

Sr. No.	Name	Mol. Wt.	% C		% H		% N		% Br		Yield in %
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	
1	ADBPBU	538	41.65	44.60	3.94	3.71	10.20	10.40	27.35	29.36	84
2	AZPBPU	580	47.60	47.63	4.45	4.51	9.61	9.66	27.15	27.21	80
3	SAPBPU	510	42.32	42.40	3.10	3.13	10.85	10.98	30.85	30.79	85
4	SBPBPU	594	48.40	48.48	4.71	4.74	9.35	9.42	26.48	26.54	75
5	SUPBPU	568	46.35	46.51	4.16	4.25	10.05	10.21	27.74	27.81	80

Table-3: IR Spectral Assignment of Ligands (cm^{-1})

No.	Name	Colour	Solubility	- NH -	- CH ₂ -	= C = O
1	ADBPBU	White	Acetone, Hot DMF, Acetic acid & ethanol	3427 (s)	2882 (w)	1655 (vs)
2	AZPBPU	White	Acetone, Hot DMF, Acetic acid & ethanol	3480 (vw)	2936 (w)	1700 (vs)
3	SAPBPU	White	Acetone, Hot DMF, Acetic acid & ethanol	3427 (w)	2937 (vw)	1606 (vs)
4	SBPBPU	White	Acetone, Hot DMF, Acetic acid & ethanol	3427 (w)	2935 (w)	1606 (w)
5	SUPBPU	White	Acetone, Hot DMF, Acetic acid & ethanol	3432 (vs)	2940 (w)	1656 (w)

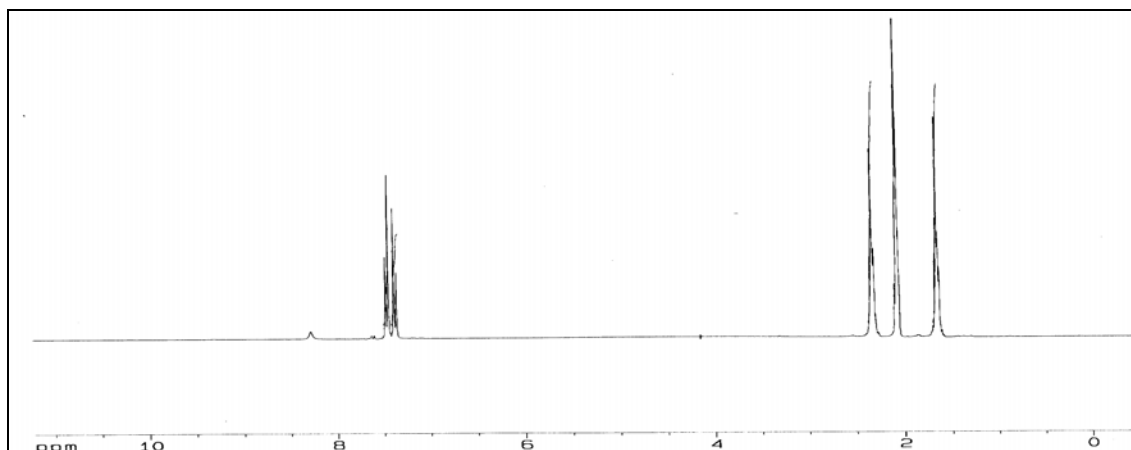


Fig.1: ¹H NMR of Ligand (ADPBPU)

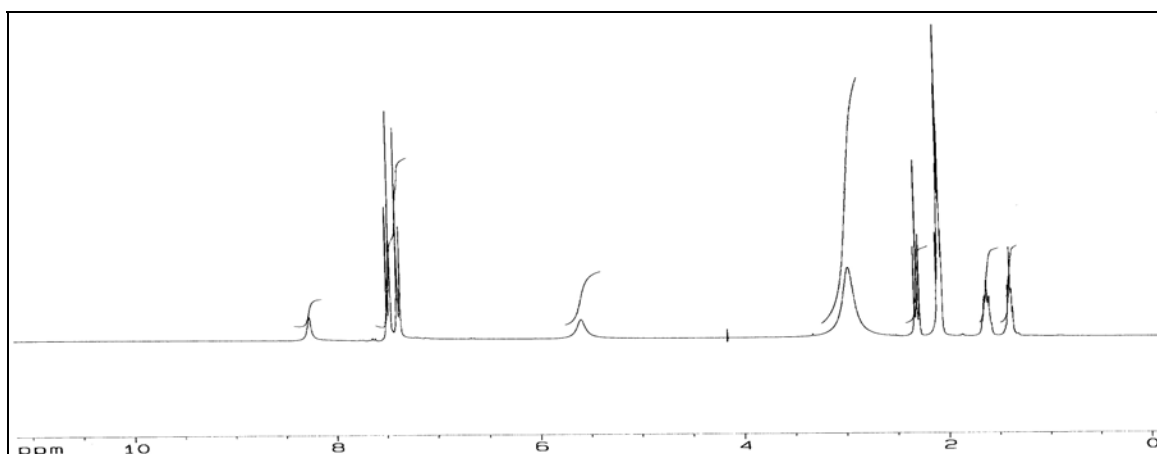


Fig.2: ¹H NMR of Ligand (AZPBPU)

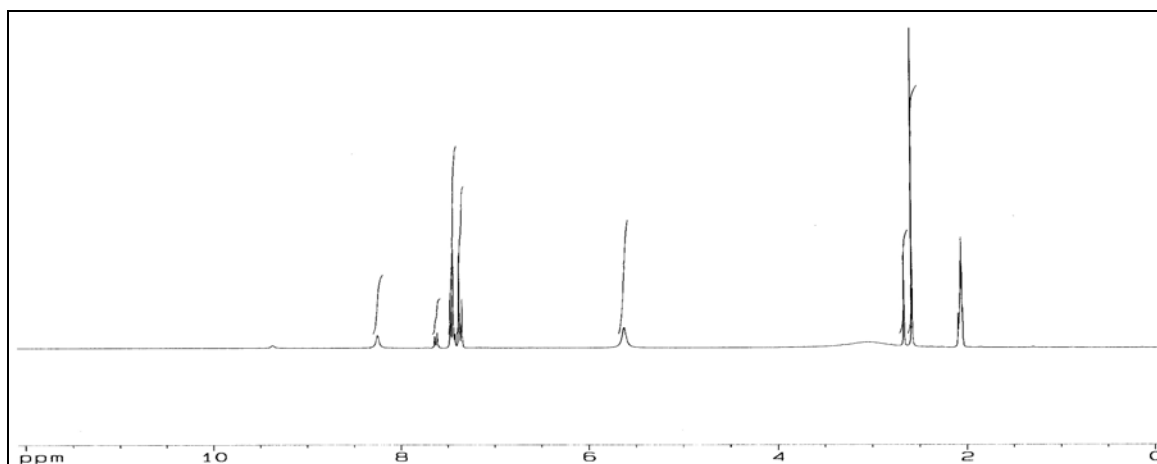


Fig.3: ¹H NMR of Ligand (SAPBPU)

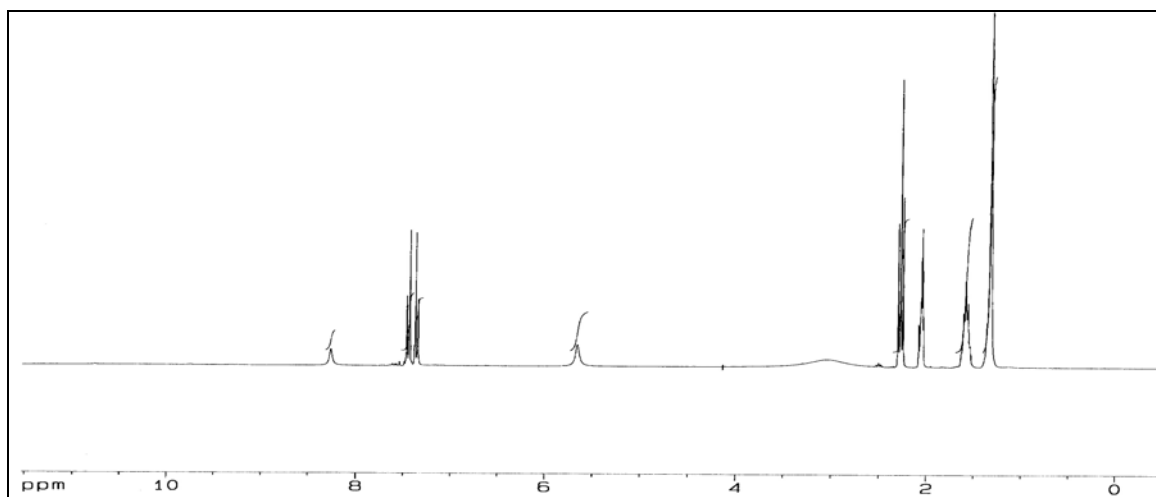


Fig.4: ¹H NMR of Ligand (SBPBPU)

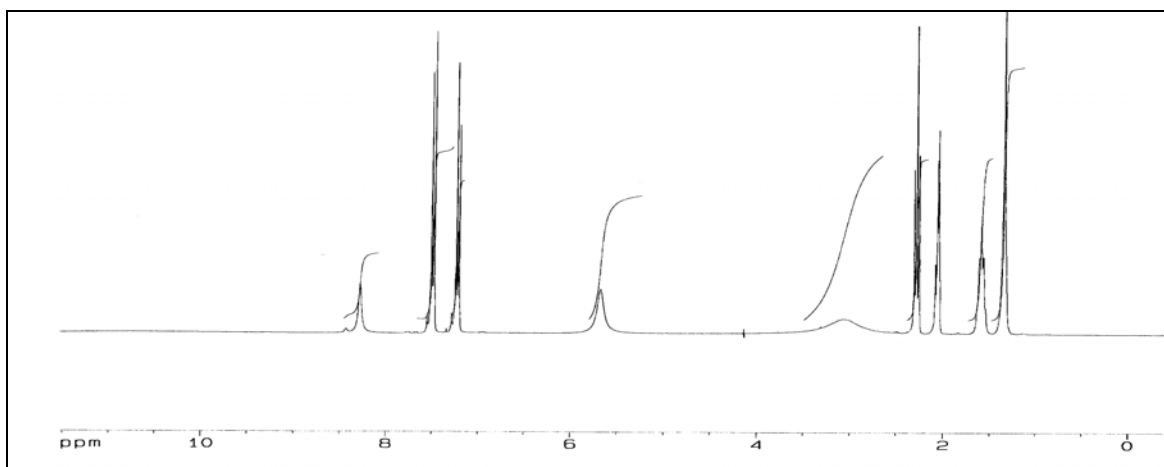


Fig.5: ¹H NMR of Ligand (SUPBPU)

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