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SPECTROSCOPIC STUDIES OF 2-AMINOETHYLAMINOMETHANEPHOSPHONIC ACID

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Abstract

Spectroscopic identifications of 2 - Aminoethylaminomethane phosphonic acid were carried out. ^{31}P *nmr, and* ^{13}C *nmr were used in the spectroscopic characterisation of the material.* ^{31}P *chemical shifts for 2 - Aminoethylaminomethanephosphonic acid in* D_2O *increase with chain length from 11.0ppm to a limiting value of ca. 27 ppm.* ^{1}H *nmr spectra were complex and difficult to employ for the assignment of structures.*

^{13}C *nmr spectra, however, provided a valuable means for identifying the aminophosphonic acid; with characteristic phosphorus-carbon coupling constants of* $^{1}J_{PC}$ *130. 1,* $^{3}J_{PCNC}$ *4-8* H_z

Introduction

The spectroscopic study of 2-aminoethylaminomethane phosphonic acid is part of concentrated research efforts in the development of new, less toxic biodegradable compounds for applications to fungicides.

The alarming rate of farm harvest losses attributed to fungi activity is one of the factors of concern to governments, industries and academic agencies, hence, research in this direction.

Problems associated with the use of organomercury compounds include the hazardous activity of mercury and its threat to human life via bioaccumulation (Riechm, 1914; Narahashi, 1997). Many organophosphorus compounds with great potentials as fungicides and pesticides have been developed in recent years (Okaya, 1966). It is important to understand the structure of these compounds in order to assess their potential as pesticides. The present spectroscopic study of 2-Aminoethylaminomethane phosphonic acid is part of efforts to achieve this objective.

Materials and Methods:

Experimental Procedure:

Preparation of 2-aminoethylaminomethanephosphonic Acid was carried out in the following stages:

- I Preparation of Chloromethanephosphonyl-dichloride
- II Preparation of Chloromethane-phosphonic acid
- III Preparation of 2-Aminoethylaminomethanephosphonic acid

Detailed preparation procedure can be obtained in earlier reports by the author (Adetunji, 1983).Nuclear Magnetic Resoneance spectra were obtained using a Perkin - Elmer R12B spectrometer at 60mHz. Chemical shifts are determined with tetramethyl silane; H_3 $P0_4$ and TSP as internal standards. Analyses for carbon, hydrogen and nitrogen were carried out using a Perkin-Elmer 240B microanalyser. Recrystallisation of 2-aminoethylaminomethanephosphonic Acid was carried out in hot methanol in order to obtain suitable crystals for X-ray structure analysis.

Results obtained include:

(a) Elemental Analysis:

Obtained (%) C = 22.78 H = 7.13 N= 17.89

Expected (%) C = 23.37 H = 7.14 N= 18.18

(b) Nuclear Magnetic Resonance spectra:
These are attached as figures 1 - 3.

Discussions

The present study of 2-Aminoethylaminomethanephosphonic acid involved structural elucidation by nuclear magnetic resonance (^{13}C, ^1H, and ^{31}P) spectroscopy (Figure 1, 2 and 3).

The ^{13}C NMR, showed a very intense peak at 39.25ppm indicating a gamma carbon attached to the terminal NH_2 groups; a doublet coupling of phosphorus alpha carbon in P-CH_2NH at 45. 68 and 52.15ppm; a doublet beta carbon coupling with phosphorus in PCH_2NHCH_2 with J = 8.9Hz (Fig. 2). The proton NMR spectra showed simple distinctive doublet of the PCH_2 group due to phosphorus coupling with the equivalent adjacent hydrogen atoms. The J_{PCH2} is

(i) ^1H (D_2O) 39.5 and 3. 8 (h, dCH_2p, ^JPCH: 12CHZ) (fig.1)

3.6 3.7 (4H, multiplet CH_2 CH_2)

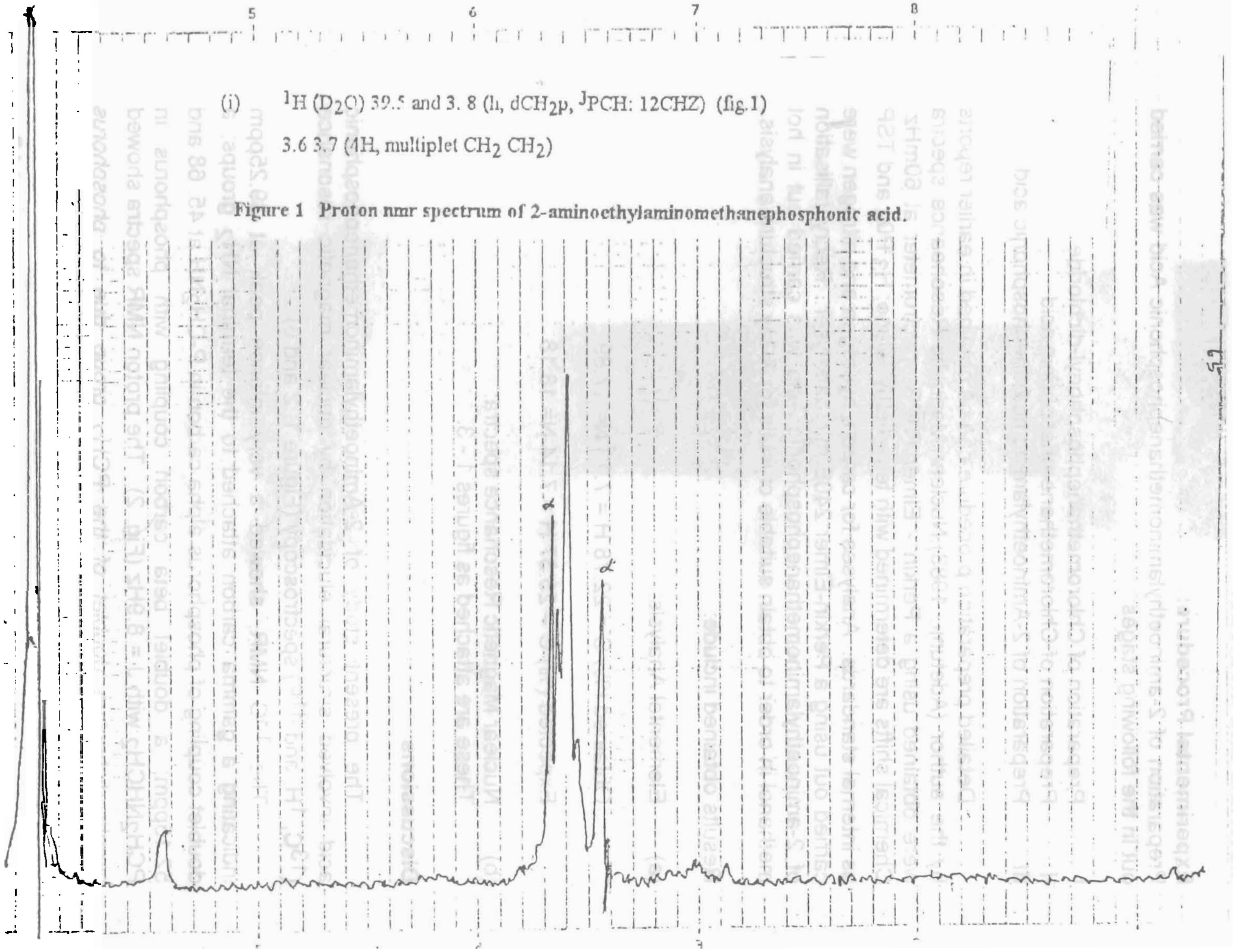
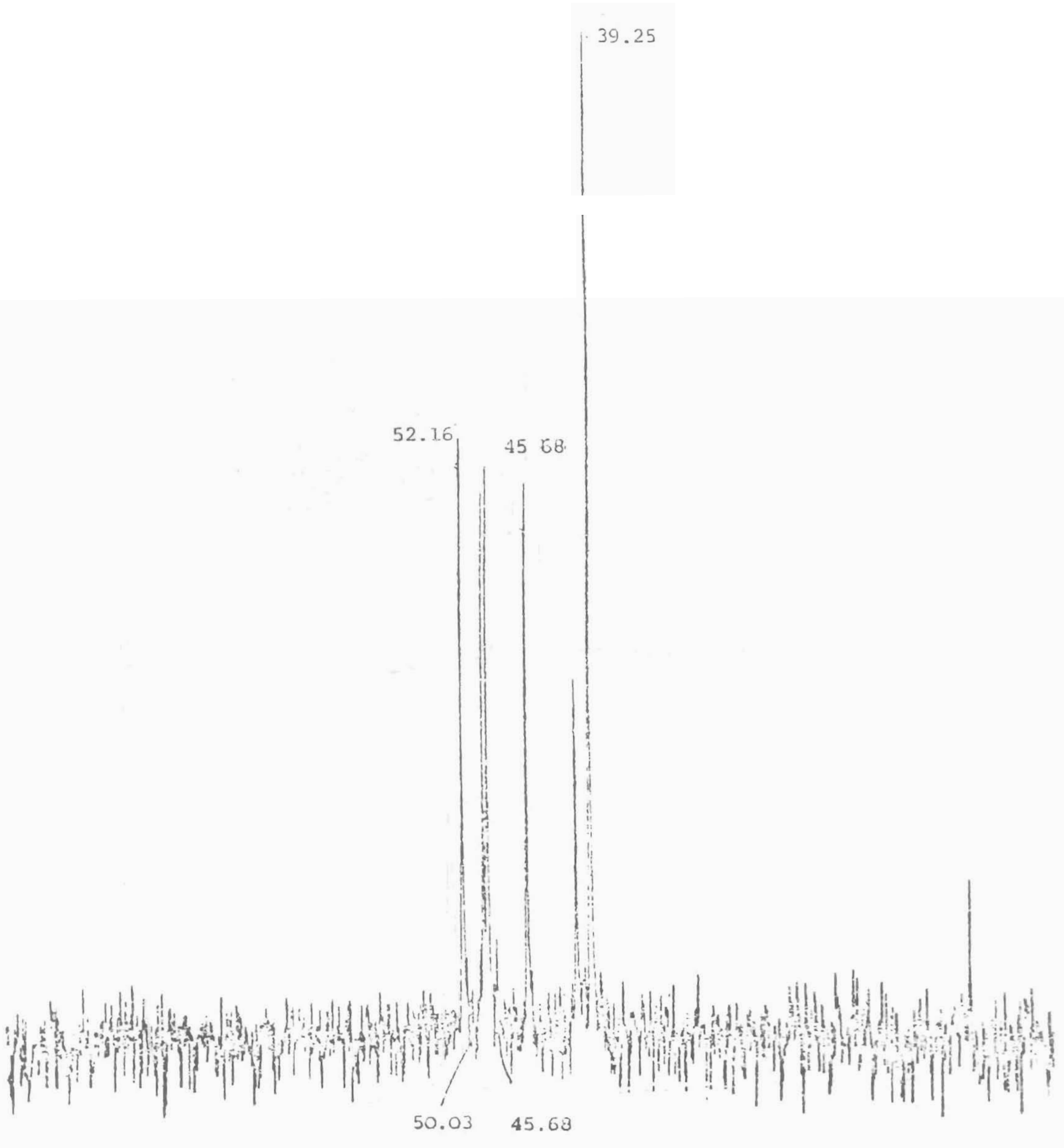


Figure 1 Proton nmr spectrum of 2-aminoethylaminomethanephosphonic acid.

(ii) ^{13}C (D_2O) 39.25 (CH_2NH_2); 48.92 (P-CH_2NH, d, J_{PCH2},130.1H_z) 49.81 (PCH_2NHCH_2, d, $^{J}NHCH_2$, 8.9H_2) (Fig.2)

Figure 2: ^{13}C nmr spectrum of 2-aminoethylaminomethanephosphonic acid



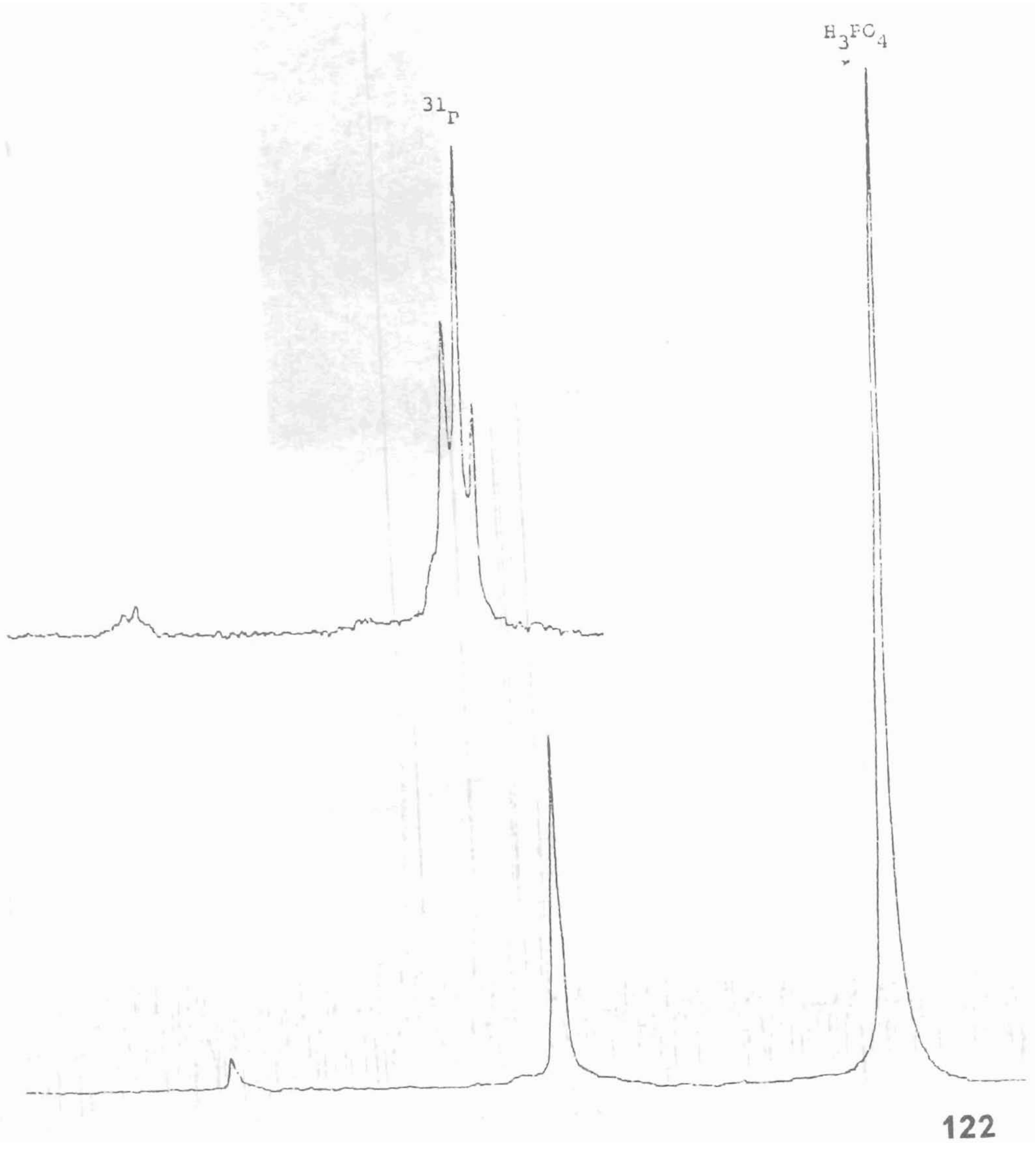
(ii) 13p (D_2O) 8.35 (t,$_2J_{HCP}$, 11.76 Hz (Fig.3)

Figure 3: ^{31}P nmr spectrum of 2-aminoethylaminomethanephosphonic acid.

Hz	ppm
258.87	7.990
282.379	8.353
270.613	8.716
258.847	9.011

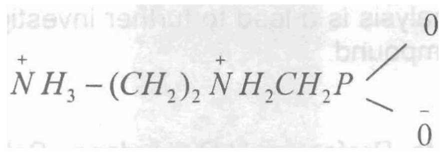
$^{31}P-H$ BB

Solvent-D_2O



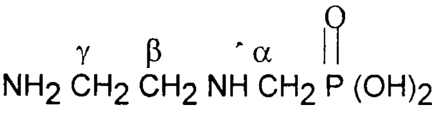
about 12H_Z, overlapping multiplets due to the methylene groups at each end of the polymethylene chain (Fig.1).

The ^{31}P NMR spectra showed characteristic triplet due to the phosphorus coupling with the two hyrogen of the methylene group given $^{2}J_{HCP}$ = 11.76 Hz (Fig.3). The elemental analysis results showed appreciable resemblance of the expected values. Like other animo acids, the omega Aminoethylaminomethanephosphonic acid exists as dipolar or zwitterionic molecule represented by



$$\overset{+}{N}H_3-(CH_2)_2\overset{+}{N}H_2CH_2P\begin{smallmatrix} \diagup 0 \\ \diagdown \bar{0} \end{smallmatrix}$$

A similar study by Horiguchi and Kandatsu (1960) and Kittredge (1962) on Aminoethanephosphonic acid showed that the NH_3 absorption band extending over the range 3300 - 2100 cm^{-1}, and the NH3 and deformation at 1658 - 1563 cm^{-1}, two broad intense bands at O1150cm^{-1} and 1044cm^{-1} assigned to $P0_2$ asymmetric and stretching modes respectively, were evidence for the dipolar character of the material . The ^{13}C NMR, confirm the reaction products obtained as the expected 2-Aminoethlaminomethanephosphonic acid by the following spectra characteristics.



$$NH_2\,\overset{\gamma}{CH_2}\,\overset{\beta}{CH_2}\,NH\,\overset{\alpha}{CH_2}\,\overset{\overset{O}{\|}}{P}\,(OH)_2$$

Three distinct peaks indicating C-atoms of different chemical environments: the gamma carbon was shown by a peak at 39.25ppm as a singlet, the beta carbon, by a peak at 49.81 as a doublet with J value = 8. 9H_Z; the alpha carbon, by a peak at 48.92ppm as a doublet with value = 130, 1H_Z (Fig.2).

The ^{31}p and ^{31}p - ^{1}H (broad band) spectra also showed the phosphorus peak at 8.53ppm and the coupling of phosphorus on the carbon atoms were revealed as a triplet with J. value = 11.76H_Z (Fig. 3) The proton N.M.R. also confirmed the coupling of phosphorus as a doublet and a multiplet on the methylene hydrogens respectively at delta = 3, 5, 3. 3.,8 ppm and 3. 6, 3. 7ppm with J. value = 12H_Z (Fig. 1)

Conclusions

The molecular structure of 2-Aminoethylaminomethane phosphonic acid has been confirmed severally by ^{13}C, ^{1}H and ^{31}P nuclear magnetic resonance spectroscopy. The melting point of the material is 278°C and the C, H, N elemental compositions as 22.78%, 7.13% and 17. 89% respectively.Suitable crystals for X-ray analysis were obtained for further investigation. It is of great interest to note the importance of the confirmation of the molecular structure of 2-Aminoethylaminomethane phosphonic acid by ^{13}C NMR; obtaining suitable crystals for the X-ray analysis is a lead to further investigations on the crystal structure of the compound.

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