

COMPARATIVE STUDIES OF PMR SPECTRA OF SOME DIHYDROPYRIDINES. PART III

A. KAMAL, TAHIRA BEGUM, M. AFROZE KHAN and ASAF A. QURESHI

PCSIR Laboratories, Karachi 39

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Comparative PMR studies of the 2,6-dimethyl-3,5-diethoxycarbonyl-4-(phenyl)-1,4-dihydropyridine (I), 2,6-dimethyl-3,5-diethoxycarbonyl-4-(2'-chlorophenyl)-1,4-dihydropyridine (II), 2,6-dimethyl-3,5-diethoxycarbonyl-4-(3'-hydroxyphenyl)-1,4-dihydropyridine (III), 2,6-dimethyl-3,5-diethoxycarbonyl-4-(4'-nitrophenyl)-1,4-dihydropyridine (IV), 2,6-dimethyl-3,5-diethoxycarbonyl-4-(3',4'-dimethoxyphenyl)-1,4-dihydropyridine (V), 2,6-dimethyl-3,5-diethoxycarbonyl-4-(α -naphthyl)-1,4-dihydropyridine (VI) are described.

In our previous communications we have described the PMR spectral studies of some isocoumarins¹, dihydropyridines and trithians.² In continuation of these studies we are describing PMR studies of some more dihydropyridines available to us.

The PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-phenyl-1,4-dihydropyridine (I) showed a triplet and a quartet centred at τ 8.85 (6H) and τ 5.6 (4H) due to an A_2B_3 system of the ethyl groups of the two ester groups, substituted at positions 3 and 5 ($J_{A_2B_3} = 7$ Hz). The two *C*-methyl groups substituted at position 2 and 6 appeared as a sharp singlet at τ 7.6 (6H). Methine proton gave a single peak at τ 4.7 (1H). The five phenyl protons being in identical environment gave a sharp peak centred at τ 2.1 (5H). Finally, the NH proton appeared at τ 0.2 (1H).

The PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-(2'-chlorophenyl)-1,4-dihydropyridine (II) showed a triplet and a quartet centred at τ 8.75 (6H) and τ 5.7 (4H) due to A_2B_3 system of the ethyls of the two ester groups, substituted at 3 and 5 positions ($J_{A_2B_3} = 7$ Hz). The two *C*-methyl groups present at 2 and 6 positions appeared as a singlet at τ 7.6 (6H) due to identical environment. The methine proton at position 4 appeared as a singlet at τ 6.2 (1H). The four benzenoid protons appeared at τ 1.9 (4H). Finally, the NH proton appeared at τ 0.5 (1H).

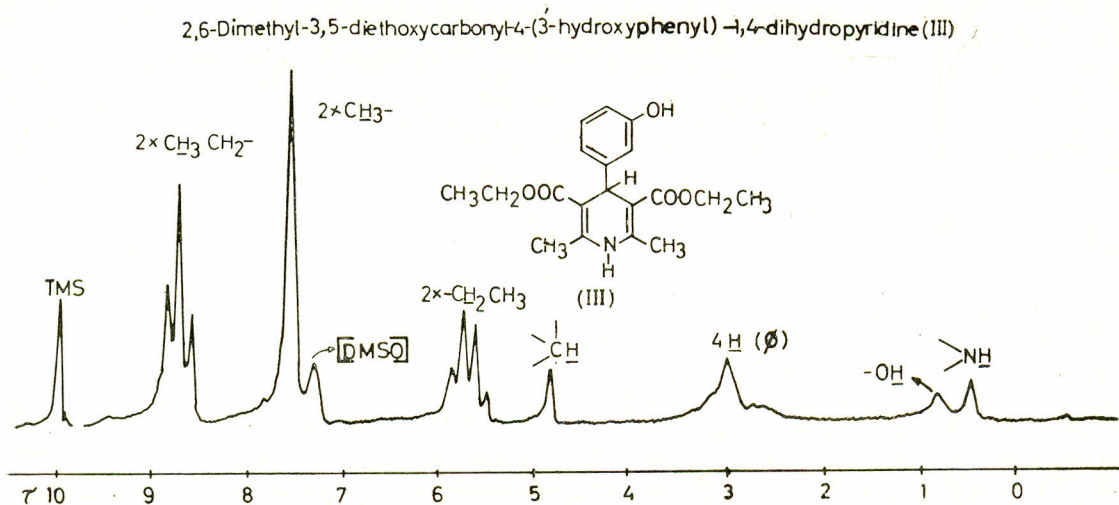
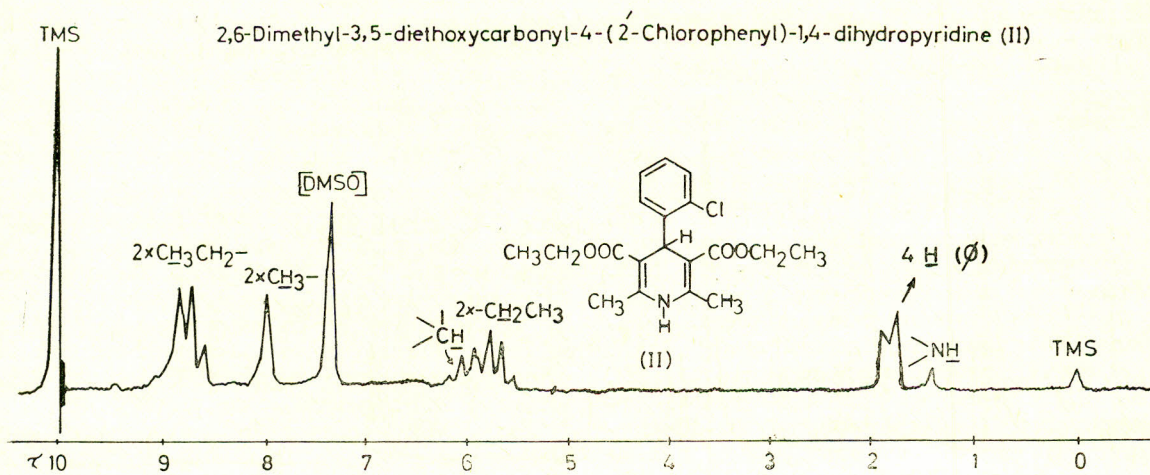
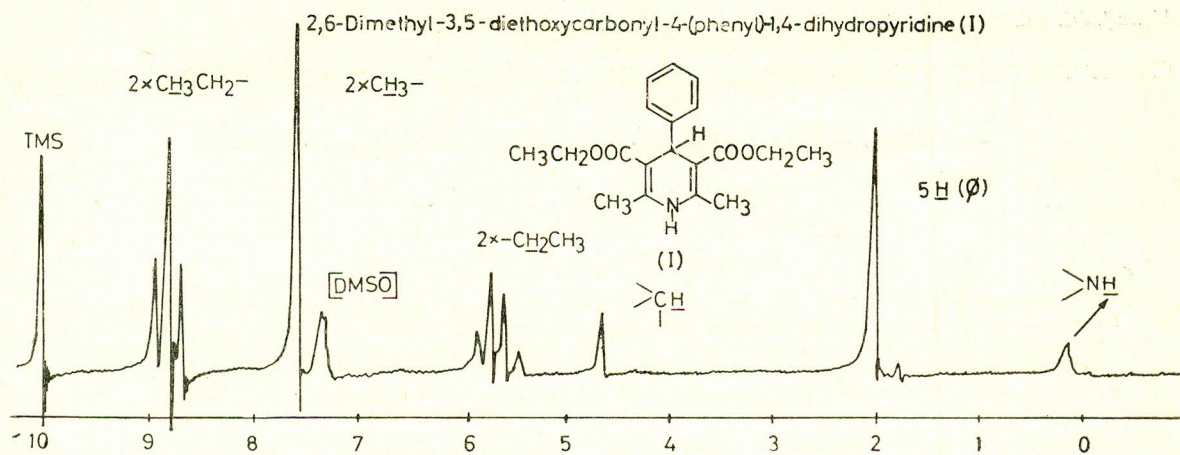
The PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-(3'-hydroxyphenyl)-1,4-dihydropyridine (III) showed a triplet and a quartet centred at τ 8.7 (6H) and τ 5.7 (4H) respectively due to A_2B_3 system of the ethyl of two ester groups substituted at 3 and 5 positions ($J_{A_2B_3} = 7$ Hz). The two *C*-methyl groups present at 2 and 6 positions as a singlet at τ 7.6 (6H) due to identical environment. The methine proton at position 4 appeared as a singlet at τ 4.75 (1H). The four benzenoid protons ap-

peared as a singlet at τ 3.0 (4H). The OH proton appeared at τ 0.8 (1H). Finally, the NH proton appeared at τ 0.5 (1H).

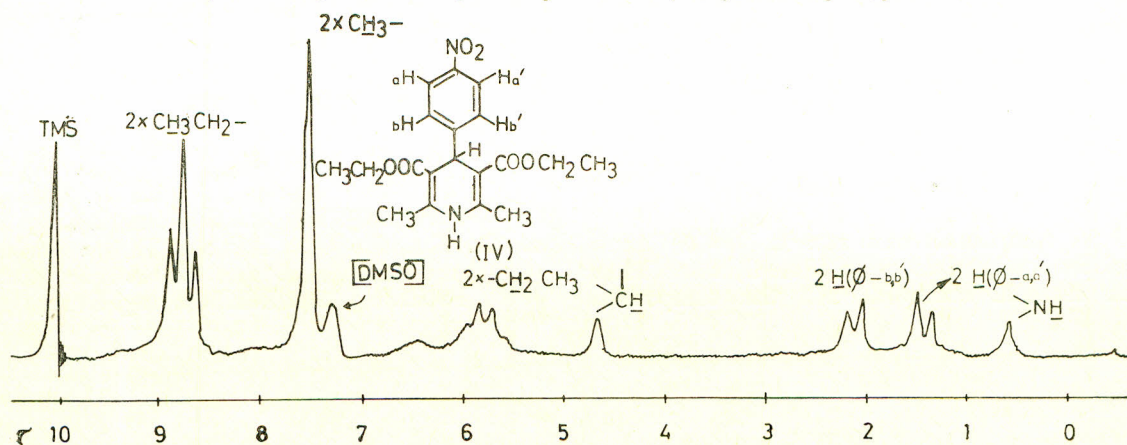
The PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-(4'-nitrophenyl)-1,4-dihydropyridine (IV) showed a triplet and a quartet centred at τ 8.75 (6H) and τ 5.8 (4H) respectively due to A_2B_3 system of the two ethyls of the two ester groups, substituted at positions 3 and 5. ($J_{A_2B_3} = 7$ Hz). The two *C*-methyl groups substituted at position 2 appeared as a sharp singlet at τ 7.55 (6H) due to identical environment. The methine proton at position 4 appeared as a singlet at τ 5.6 (1H). The four benzenoid protons appeared as two doublets centred at τ 2.12 (2H; *bb'*) and τ 1.38 (2H; *aa'*) showing *ortho* coupling (7 Hz). The *aa'* protons appeared at lower τ value due to the neighbouring NO_2 group. The proton of NH appeared at τ 0.5 (1H).

The PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-(3',4'-dimethoxyphenyl)-1,4-dihydropyridine (V) showed a triplet and a quartet centred at τ 8.75 (6H) and τ 5.7 (4H) due to A_2B_3 system of the ethyls of two ester groups, substituted at the 3 and 5 positions ($J_{A_2B_3} = 7$ Hz). The two *C*-methyl groups present at 2 and 6 positions appeared as a singlet at τ 7.6 (6H) being in identical environment. The two $-OCH_3$ groups being in identical environment appeared as a sharp singlet at τ 6.05 (6H). The methine proton at position 4 appeared as a singlet at τ 4.82. The three benzenoid protons appeared as a doublet centred at τ 2.67 (3H) showing *meta* coupling ($J = 3$ Hz). Finally, the NH proton appeared at τ 0.5 (1H).

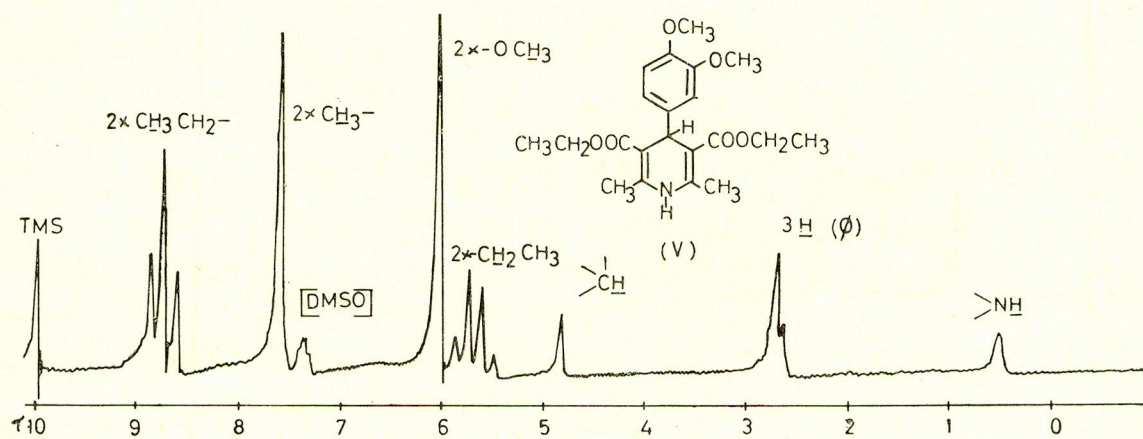
The PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-(α -naphthyl)-1,4-dihydropyridine (VI) showed a triplet and a quartet centred at τ 9.1 (6H) and τ 5.7 (4H) due to A_2B_3 system of the ethyls of the two ester groups, substituted at positions 3 and 5 ($J_{A_2B_3} = 7$ Hz). The two *C*-methyls substituted at positions 2 and 6 appeared as a sharp singlet at τ 7.52 (6H).



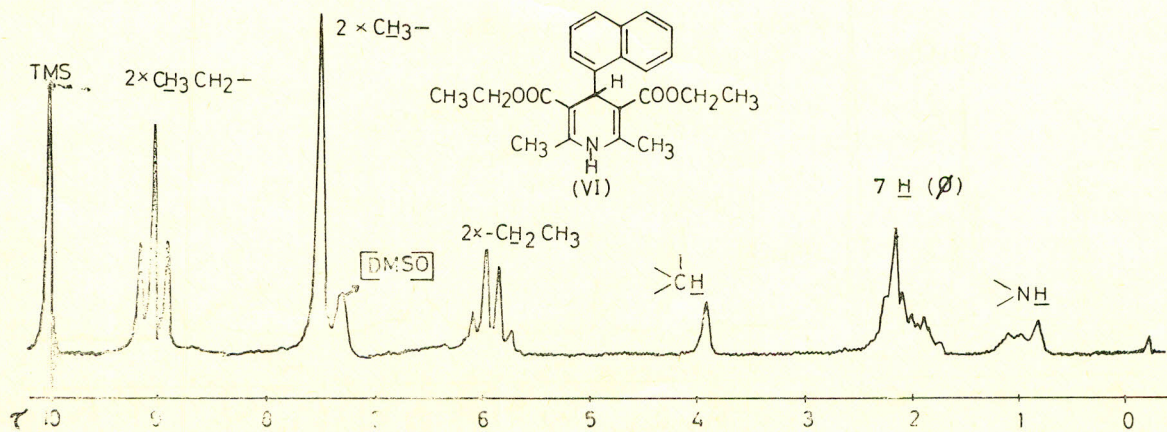
2,6-Dimethyl-3,5-diethoxycarbonyl-4-(4'-nitrophenyl)-1,4-dihydropyridine (IV)



2,6-Dimethyl-3,5-diethoxycarbonyl-4-(3,4-dimethoxyphenyl)-1,4-dihydropyridine (V)



2,6-Dimethyl-3,5-diethoxycarbonyl-4-(α -naphthyl)-1,4-dihydropyridine (VI)



Methine proton gave a sharp peak at τ 3.9 (1H), this lower value is due to the presence of the neighbouring naphthyl group. The seven naphthyl protons appeared between τ 1.7~2.4 (7H). The proton of the >NH group gave a singlet at τ 0.8 (1H), thus accounting for all the protons in the molecule.

Experimental

All the compounds were run on DP-60 Varian Associates NMR machine in DMSO, using TMS as an internal standard. All the compounds

were run in DMSO (d_6) due to their low solubility in other solvents. The concentration of the each compound was about 11-15%.

References

1. A. Kamal, Nilofer Kazi, Tahira Begum, M. Afroze Khan and Asaf A. Qureshi, Pakistan J. Sci. Ind. Res., **14**, 1 (1971).
2. A. Kamal, Rafia Akhtar, Tahira Begum, Asaf A. Qureshi and M. Afroze Khan, Pakistan J. Sci. Ind. Res., **14**, 6 (1971).