

## COMPARATIVE STUDIES OF PROTON MAGNETIC RESONANCE OF SOME DIHYDROPYRIDINES AND TRITHIANS. PART II

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The PMR of 2,6-dimethyl-3,5-diethoxycarbonyl-4-formyl-1,4-dihydropyridine (I), 2,4,6-trimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridine (II), 2,4,6-trimethyl-3,5-diethoxycarbonyl-4-propyl-1,4-dihydropyridine (III), 2,6-dimethyl-3,5-diethoxycarbonyl-4-(4'-methoxyphenyl)-1,4-dihydropyridine (IV), 2,6-dimethyl-3,5-diethoxy-carbonyl-4-(3'-methoxy-4'-hydroxyphenyl)-1,4-dihydropyridine (V), 2,6-dimethyl-3,5-diethoxycarbonyl-4-styryl-1,4-dihydropyridine (VI), 2,6-dimethyl-3,5-diethoxycarbon-4-furyl-1,4-dihydropyridine (VII), 2,4,6-tri-(4'-methoxyphenyl)-1,3,5-trithian (VIII) and 2,4,6-tri-(2',3'-dimethoxyphenyl)-1,3,5-trithian (IX) has been studied.

In earlier communications the syntheses of substituted dihydropyridines<sup>1</sup> and a number of substituted trithians<sup>2</sup> in aqueous medium were reported alongwith their UV and IR absorption data. Since these compounds were still available, it was felt of interest to undertake their PMR studies. All these compounds were run in DMSO ( $d_6$ ) due to their low solubility in other solvents.

The PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-formyl-1,4-dihydropyridine (I) showed a triplet and a quartet centred at  $\tau$  8.78 (6H) and  $\tau$  5.75 (4H) due to  $A_2B_3$  system of the ethyls of the two ester groups substituted at the 3 and 5 positions ( $J_{A_2B_3}$  7 c/s). The two methyl groups present at 2 and 6 positions appeared as a singlet at  $\tau$  7.76 for the two C-methyl groups. The two *geminal* protons present at position 4 showed two doublets centred at  $\tau$  3.8 and  $\tau$  3.6 ( $J$  2 c/s). Finally, the remaining NH proton appeared at  $\tau$  2.3.

The PMR spectrum of 2,4,6-trimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridine (II) showed a doublet and a quartet centred at  $\tau$  9.49 (3H)  $CH_3-CH$  and  $\tau$  6.04 (H,  $CH_3-CH$ ;  $J_{AB_3}$  7.3 c/s). A triplet and a quartet appeared at  $\tau$  8.62 (6H); and  $\tau$  5.7 (4H) due to  $A_2B_3$  system of the two ethyls of the ester groups ( $J_{A_2B_3}$  7.3 c/s). The two C-methyl groups at 2 and 6 positions being under identical environments appeared as a singlet at  $\tau$  7.62 (6H). Finally the remaining proton (NH) appeared at  $\tau$  0.82.

The PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-propyl-1,4-dihydropyridine (III) showed an ill-defined triplet centred at  $\tau$  9.2 (3H) for C-methyl attached to a series of methylene groups, as in long chain aliphatic compounds.<sup>3</sup> There was an ill-defined triplet centred at  $\tau$  8.7 (10H) for the protons of two C-methyl of the ester groups and two methylene groups of the side chain. The 2,6-dimethyl groups

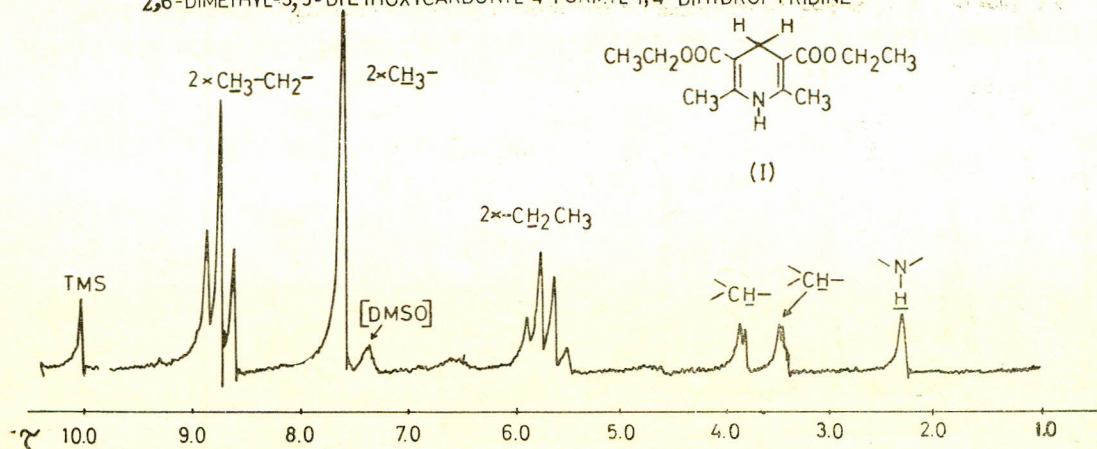
appeared as singlet at  $\tau$  7.7 (6H). There was a triplet centred at  $\tau$  6.2 (1H) due to the methine proton at position 4. A quartet centred at  $\tau$  5.7 (4H) due to  $A_2B_3$  system for protons of the two methylene groups of the ethyl ester ( $J_{A_2B_3}$  7 c/s). The last proton for  $>NH$  appeared at usual place at  $\tau$  0.8 (1H) as was observed in the previous two cases.

PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-(4'-methoxyphenyl)-1,4-dihydropyridine (IV) showed a triplet at  $\tau$  8.79 for the two methyls of the two ethoxycarbonyl groups (6H;  $CH_3-CH_2$ ;  $J_{A_2B_3}$  7.3 c/s) and a quartet at  $\tau$  5.62 (4H;  $CH_3-CH_2$ ;  $J_{A_2B_3}$  7.3 c/s). A singlet at  $\tau$  4.66 (1H) appeared for the proton at 4 position of the dihydropyridine ring. The two C-methyl groups at 2 and 6 positions appeared as a singlet at  $\tau$  7.6 (6H). The signal for the three O- $CH_3$  protons appeared at  $\tau$  6.26 (3H). The four benzenoid protons appeared as a double doublet at  $\tau$  2.58 and  $\tau$  2.18 for four benzenoid protons ( $J$  10 c/s, *ortho*-coupling; and  $J$  1.8 c/s, *meta*-coupling). Finally the  $>NH$  proton signal appeared at  $\tau$  0.27 (1H).

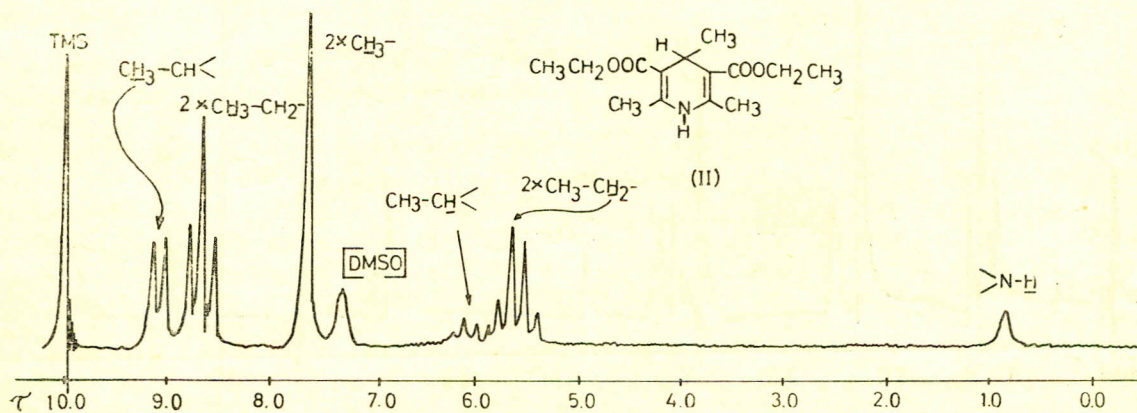
The PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-(3'-methoxy-4'-hydroxyphenyl)-1,4-dihydropyridine (V) showed a triplet and a quartet centred at  $\tau$  8.78 (6H) and  $\tau$  5.98 (4H) for the two ethyls of the ethyl ester groups at positions 3 and 5. The two methyl groups at positions 2 and 6 appeared as a singlet at  $\tau$  7.7 (6H). The protons of *O*-methyl ether group appeared at  $\tau$  6.25 (3H) as a sharp singlet. The methine proton substituted at position 4 appeared as a singlet at  $\tau$  5.1 (1H). The benzenoid protons appeared as a double doublet centred at  $\tau$  3.32 (2H;  $H_a, H_b$ ) and  $\tau$  1.35 (1H;  $H_c$ ) showing *ortho*- and *meta*-coupling with each other  $J$  8 and 2 c/s. The proton of OH and NH appeared as sharp singlet at  $\tau$  2.55 (1H) and  $\tau$  0.6 (1H) respectively.



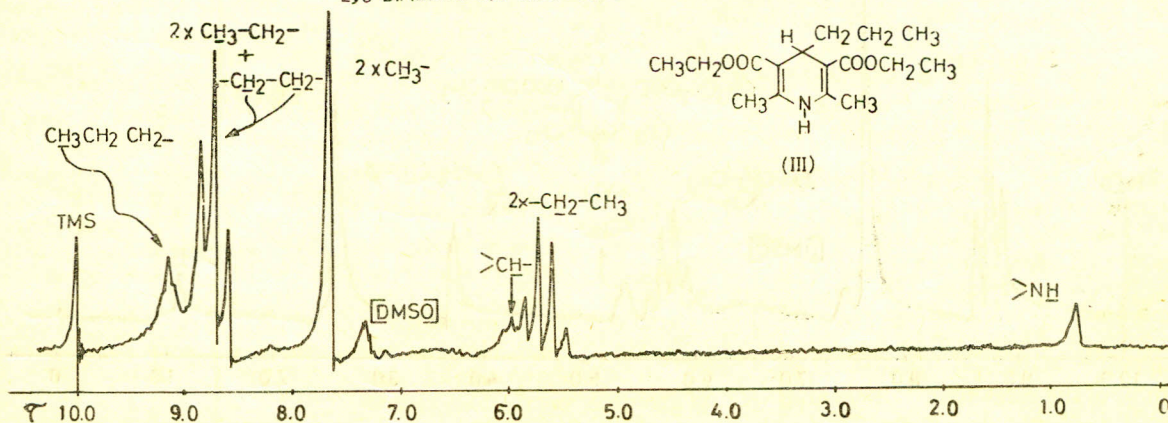
2,6-DIMETHYL-3,5-DIETHOXYCARBONYL-4-FORMYL-1,4-DIHYDROPYRIDINE



2,4,6-TRIMETHYL-3,5-DIETHOXYCARBONYL-1,4-DIHYDROPYRIDINE

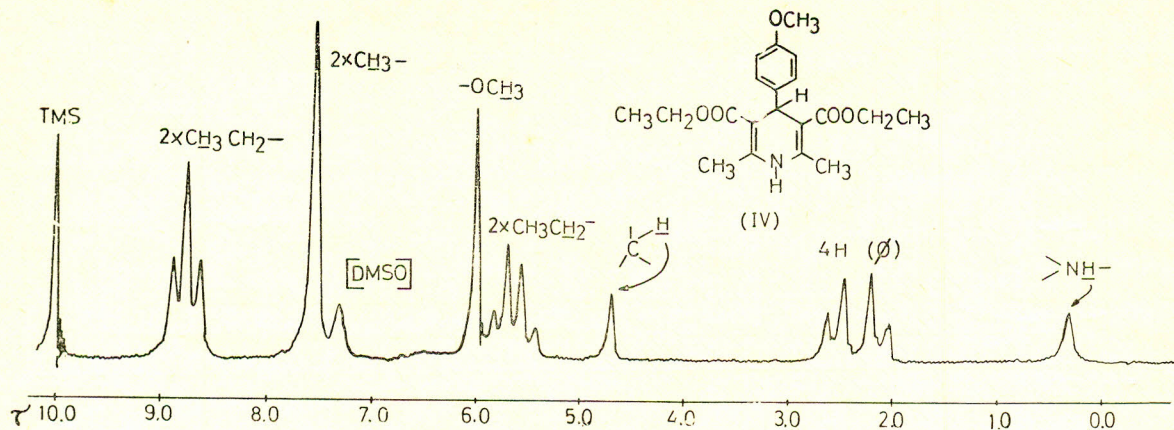


2,6-DIMETHYL-3,5-DIETHOXYCARBONYL-4-PROPYL-1,4-DIHYDROPYRIDINE

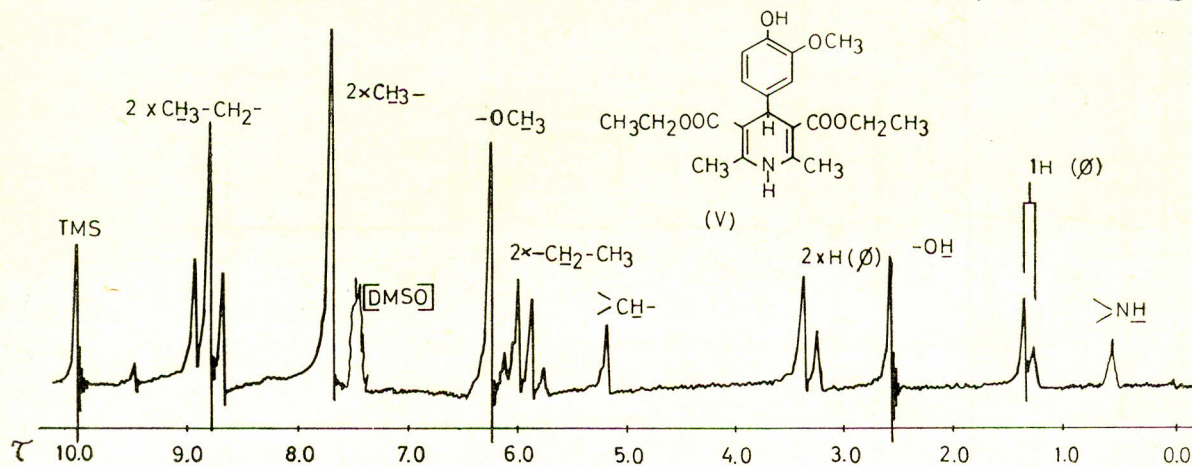




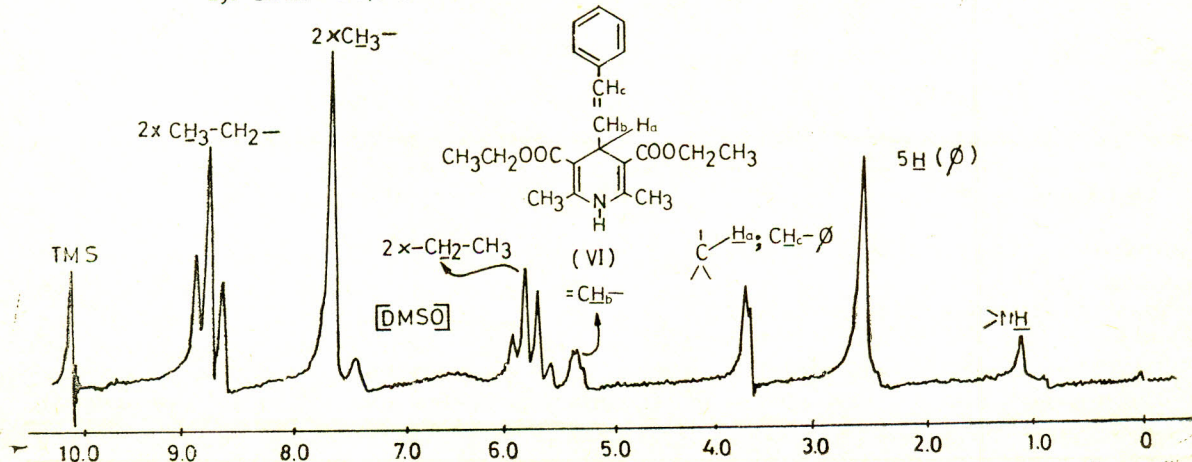
## 2,6-DIMETHYL-3,5-DICARBETHOXY-4-(4-METHOXY PHENYL)-1,4-DIHYDROPYRIDINE



## 2,6-DIMETHYL-3,5-DIETHOXYCARBONYL-4-(3'-METHOXY-4'-HYDROXYPHENYL)-1,4-DIHYDROPYRIDINE

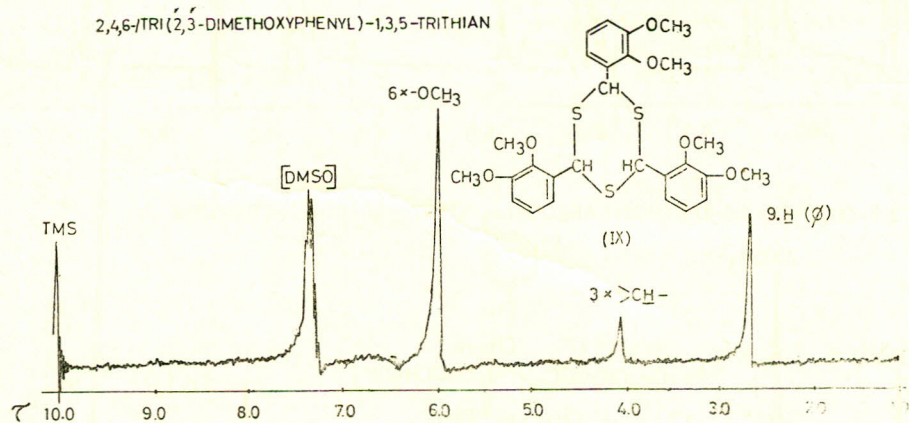
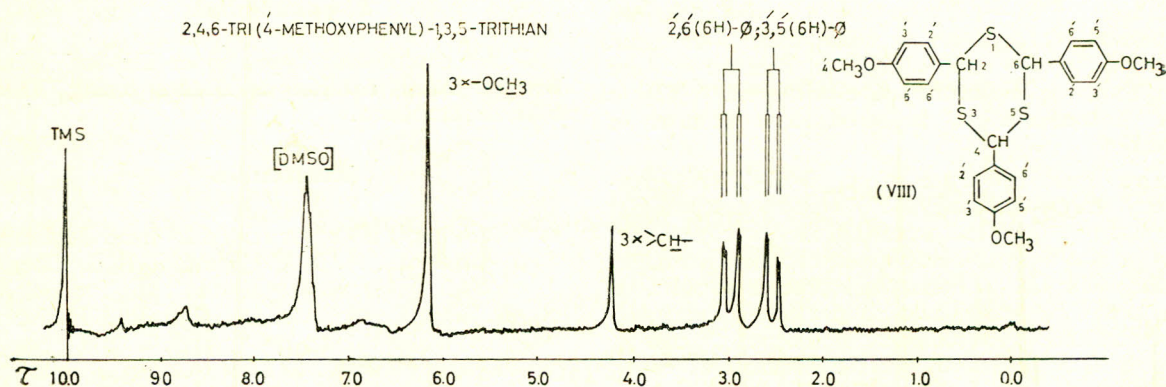
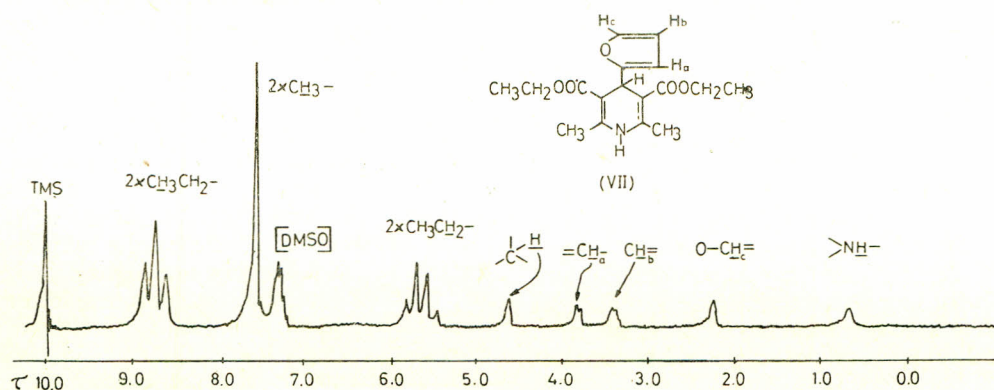


## 2,6-DIMETHYL-3,5-DIETHOXYCARBONYL-4-STYRYL-1,4-DIHYDROPYRIDINE





## 2,6-DIMETHYL-3,5-DIETHOXYCARBONYL-4-FURYL-1,4-DIHYDROPYRIDINE



The PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-styryl-1,4-dihydropyridine (VI) showed a triplet and quartet centred at  $\tau$  8.9 (6H) and  $\tau$  5.8 (4H) due to  $A_2B_3$  system of the two ethyl groups at 3 and 5 positions ( $J_{A_2B_3}$  7 c/s). The two methyl groups substituted at positions 2 and 6 appeared as singlet at  $\tau$  7.7 (6H). There was a double doublet centred at  $\tau$  5.35 due to proton  $H_b$  coupling with  $H_a$  and  $H_c$ .

The protons  $H_a$  and  $H_c$  showed a superimposed doublet centred at  $\tau$  3.8 (2H;  $J$  1 c/s) due to the nearly identical environment. All these protons ( $H_a$ ,  $H_b$ ,  $H_c$ ) were in *cis*-configuration due to the coupling constant,  $J$  2 c/s. respectively. The five benzenoid protons appeared as a sharp singlet at  $\tau$  2.7 (5H). The proton of NH appeared at  $\tau$  1.1 (1H), thus accounting for all the protons in the molecule.



PMR spectrum of 2,6-dimethyl-3,5-diethoxycarbonyl-4-furyl-1,4-dihydropyridine (VII) showed a triplet and a quartet at  $\tau$  8.68 (6H;  $2 \times \text{CH}_3\text{—CH}_2\text{—}$ ) and a quartet at  $\tau$  5.64 (4H;  $2 \times \text{CH}_3\text{—CH}_2\text{—}$ ) due to a  $A_2B_3$  system ( $J_{A_2B_3}$  7.3 c/s). A singlet appeared at  $\tau$  7.6 for the two  $\text{CH}_3$  groups in identical environment at 2 and 6 positions of the dihydropyridine ring and a singlet at  $\tau$  4.62 (1H) appeared for the proton at 4 position of the same ring. Two doublets at  $\tau$  3.8 (1H) and  $\tau$  3.4 (1H) for the two protons  $H_a$  and  $H_b$  in the furan ring and a signal at  $\tau$  2.3 (singlet 1H) appeared for the proton  $H_c$  of the same ring. Finally, the *NH* proton signal appeared as usual at  $\tau$  0.64

In all the above-discussed substituted dihydropyridines the  $\text{—CH}_3$  at the  $\alpha$  and  $\alpha'$  positions appeared at a lower  $\tau$  value than its usual position ( $\tau=8\sim 10$ ). This is because of the neighbouring electronegative nitrogen. This is not uncommon as reported in a number of cases.<sup>3,4</sup>

The PMR spectrum of 2,4,6-tri-(4'-methoxyphenyl)-1,3,5-trithian(VIII) showed a sharp singlet at  $\tau$  6.15 (9H) for the protons of the three methoxyl groups due to their being in identical environment in the molecule. The methine protons at positions 2, 4 and 6 appeared as a singlet at  $\tau$  4.25 (3H). The benzenoid protons at positions 3' and 5' appeared as ill-defined double doublets at  $\tau$  2.5 showing *ortho* and *meta*-coupling ( $J$  8 and 1.5 c/s respectively). The protons at positions 2' and 6' appeared as ill-defined double doublets centred at  $\tau$  3.0 showing *ortho* and *meta*-coupling ( $J$  8 and 1.5 c/s respectively).

The PMR spectrum of 2,4,6-tri-(2',3'-dimethoxyphenyl)-1,3,5-trithian (IX) showed a sharp singlet at  $\tau$  6.1 (18H) for six methoxyl groups due to their identical environment in the molecule. The methine protons at positions 2, 4 and 6 appeared as a singlet at  $\tau$  4.1 (3H). Finally, all the benzenoid protons appeared as a sharp singlet at  $\tau$  2.7 due to the symmetry of the molecule, thus accounting for all the protons in the molecule.

The above PMR studies of the dihydropyridine compounds showed very fine signals and splitting for protons present in this molecule. The benzenoid protons in the two trithians studied showed sharp signals due to their being in identical environment on the three benzene rings.

### Experimental

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

### References

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