

COMPARATIVE STUDIES OF PROTON MAGNETIC RESONANCE OF SOME SUBSTITUTED SKATYL MANNICH BASES AND RELATED COMPOUNDS. PART V

A. KAMAL, YASMEEN HAIDER, NILOFER QURESHI and ASAF A. QURESHI

PCSIR Laboratories, Karachi 39

(Received January 22, 1971)

The study of the PMR spectra of *N*-skatylpyrrolidine (I), *N*-skatylpiperidine (II), *N*-skatylisatin (III), *N,N*-diskatylpiperazine (IV), *N*-skatyl- α -naphthylamine (V), skatyl (phenanthroyl-2)-methane (VI), β -morpholinethyl-2-phenanthroyl ketone hydrochloride (VII), and 1-indolylbutan-3-one (VIII) have been described.

In the previous communications¹⁻⁴ the PMR studies of different types of compounds such as isocoumarins, dihydropyridines, trithians, di-indolylmethanes and many other natural products have been described. All the above studies of these compounds had revealed the fine splitting and coupling constants of benzenoid protons at *ortho* and *meta* positions. In the present communication PMR studies of substituted skatyl Mannich bases and related compounds have been described in detail. All these compounds were recorded in DMSO (d_6) due to the low solubility in $CDCl_3$.

The PMR spectrum of *N*-skatylpyrrolidine (I) showed an ill-defined superimposed sextet, centred at τ 8.35 (4H) accounting for two methylene groups at β and β' positions in the pyrrole ring. A sharp singlet appeared at τ 6.65 (2H) for a methylene group (a) of the skatyl moiety. The four protons of the two methylene groups adjacent to the nitrogen atom appeared as a singlet at τ 6.35 (4H). This slightly low chemical shift was due to the shielding effect of nitrogen atom. The α -proton of the indole group appeared as a doublet, centred at τ 3.15 (1H; 8 Hz). The benzenoid protons appeared as a multiplet, centred at τ 2.9 (4H). Finally the proton for $>NH$ group appeared as a doublet, centred at τ 2.5 (1H; 8 Hz), thus accounting for all the sixteen protons present in the molecule.

The PMR spectrum of *N*-skatylpiperidine (II) showed a sharp singlet at τ 8.45 (6H) for three methylene groups (α, α', β) of piperidine ring. The protons of the methylene group (a) of skatyl moiety appeared as a singlet at τ 6.43 (2H). The four protons of the two methylene groups (α, α') adjacent to nitrogen atom showed a sharp singlet at τ 6.28 (4H). The α -proton of the indole group (b) appeared as a doublet centred at τ 2.91 (1H; 8 Hz). The benzenoid protons appeared as a multiplet, centred at τ 2.62 (4H). The remaining proton of the $>NH$ group appeared as a doublet centred at τ 2.25 (1H; 8 Hz).

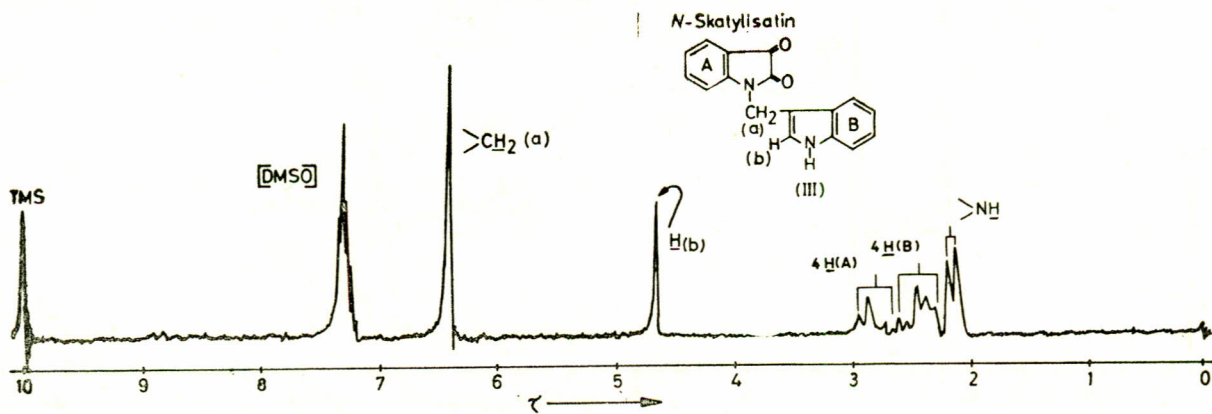
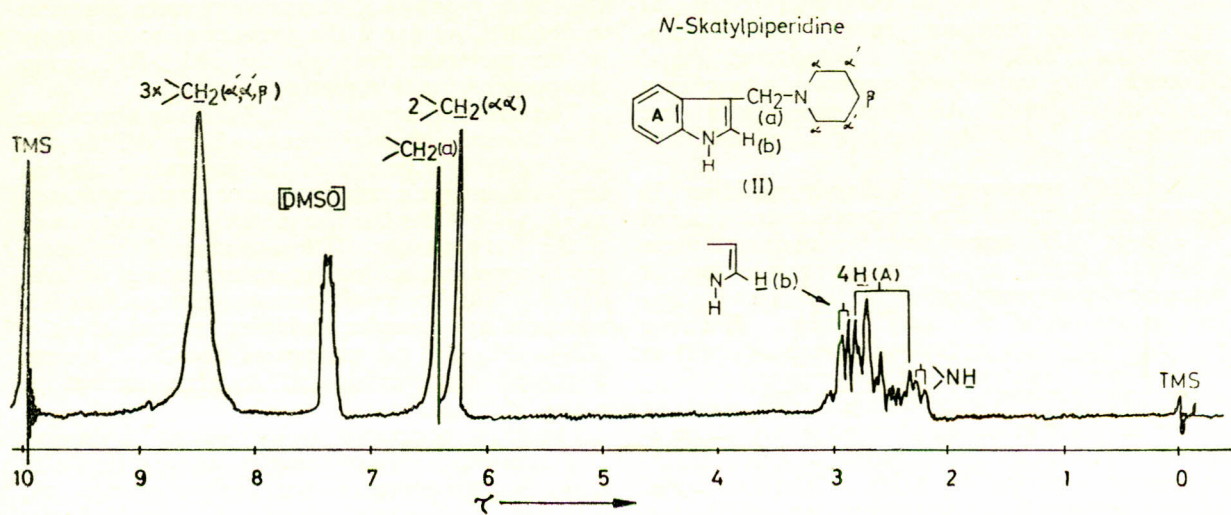
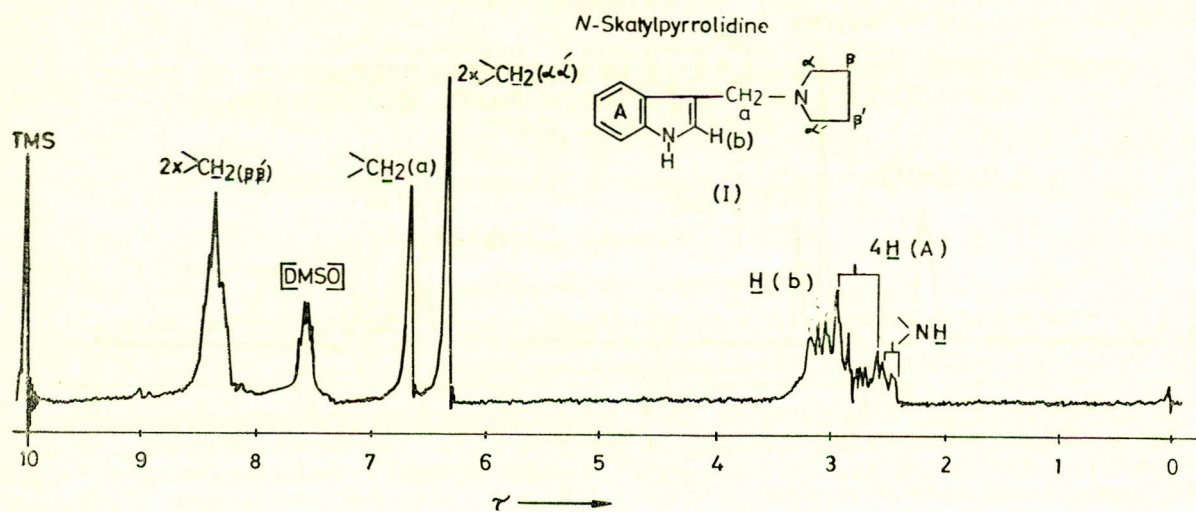
The PMR spectrum of *N*-skatylisatin (III), showed a sharp singlet at τ 6.42 (2H) for the methylene group of indole moiety. The α -proton of

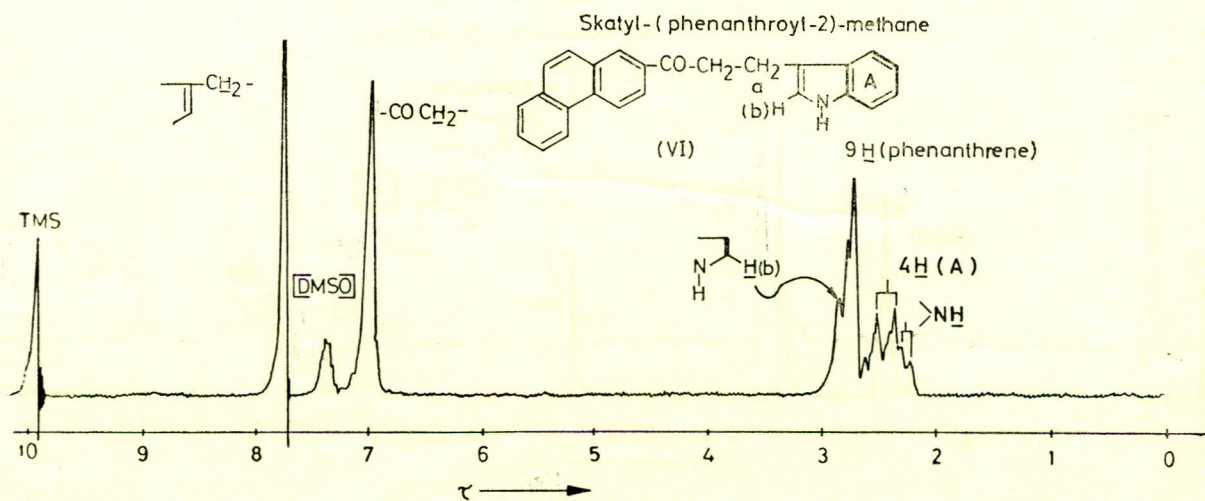
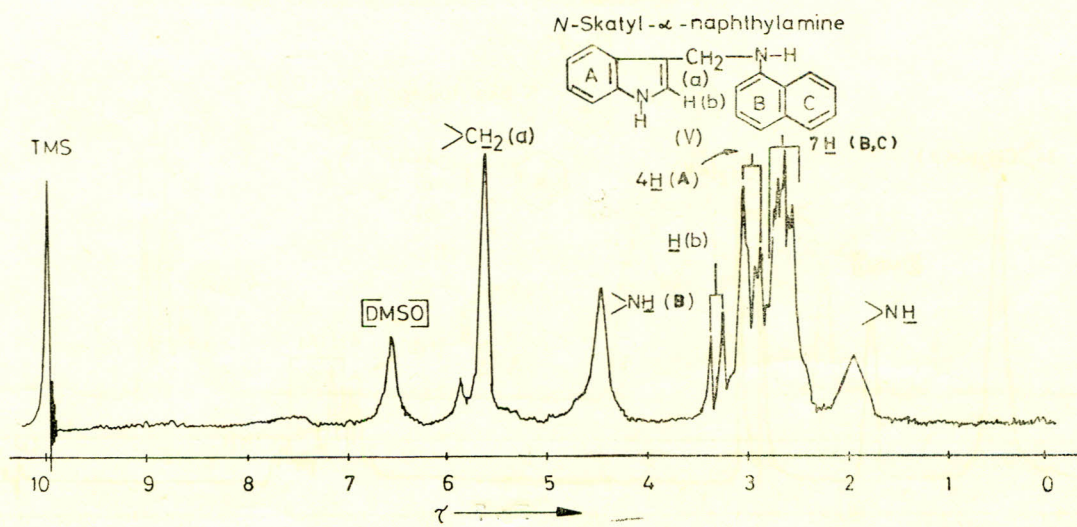
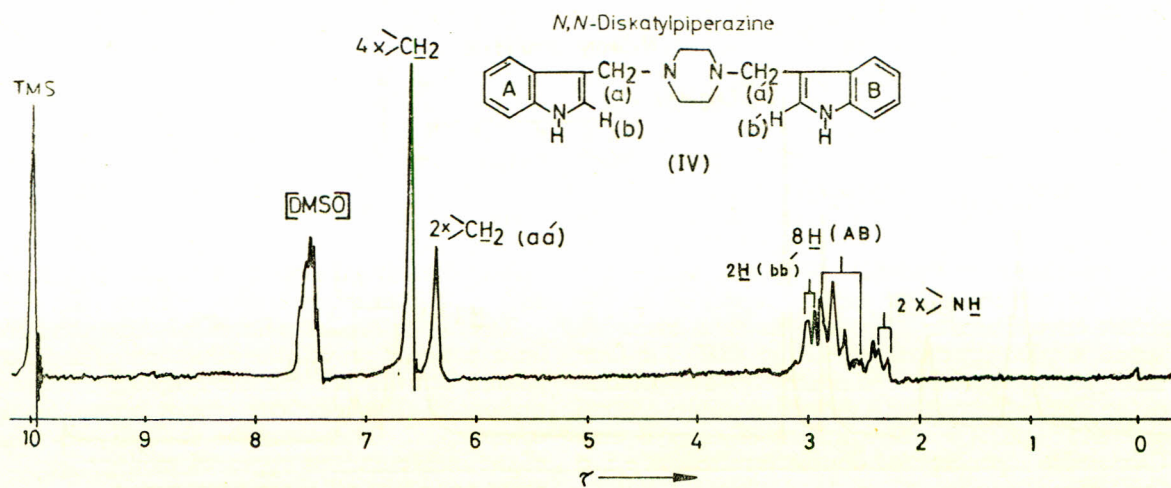
the indole group (b) appeared as a sharp singlet at τ 4.72 (1H). The benzenoid protons of ring A and B appeared as multiplets centred at τ 2.75 (4H) and τ 2.55 (4H) respectively. Finally the proton of the $>NH$ group appeared as a doublet centred at τ 2.26 (1H; 8 Hz). The α -proton of the indole group in all the previous cases appeared as doublets but due to the presence of isatin moiety in the molecule the coupling with $>NH$ group disappeared for this proton.

The PMR spectrum of *N,N*-diskatylpiperazine (IV) showed a sharp singlet at τ 6.57 (8H) for the four methylene groups of the piperazine ring in identical environments. Another singlet appeared at τ 6.34 (4H) for the two methylene groups (a,a) of the skatyl moiety. The α -protons of the indole group appeared as doublet centred at τ 2.98 (2H; 8 Hz). The benzenoid protons of rings A and B appeared as a complex multiplet centred at τ 2.7 (8H). Finally, the protons of the $>NH$ groups appeared as superimposed doublets centred at τ 2.3 (2H; 8 Hz).

The PMR spectrum of *N*-skatyl- α -naphthylamine (V) showed a sharp singlet at τ 5.63 (2H) indicating the presence of methylene group (a), attached to a hetero atom. A broad singlet appeared at τ 4.5 (1H) due to the presence of $>NH$ group attached to the benzene ring. The α -proton (b) of the indole ring appeared as a doublet centred at τ 3.32 (1H; 8 Hz). In the benzenoid region, there was a multiplet centred at τ 2.95 (4H), indicating the protons of the benzene ring A. Another multiplet appeared at τ 2.62 (7H) indicating the presence of all the protons present in the naphthalene ring B and C. A broad singlet appeared at τ 1.98 (1H) due to the presence of $>NH$ group of indole moiety, thus accounting for all the protons in the molecule.

The PMR spectrum of skatyl-(phenanthroyl-2)-methane (VI) showed a sharp singlet at τ 7.75 (2H) due to the presence of a methylene group (a) in the molecule. The protons of another methylene group appeared at a somewhat lower τ value as a sharp singlet at τ 7.0 (2H) due to the presence of a carbonyl group in the adjacent position. The α -proton (b) of the indole moiety



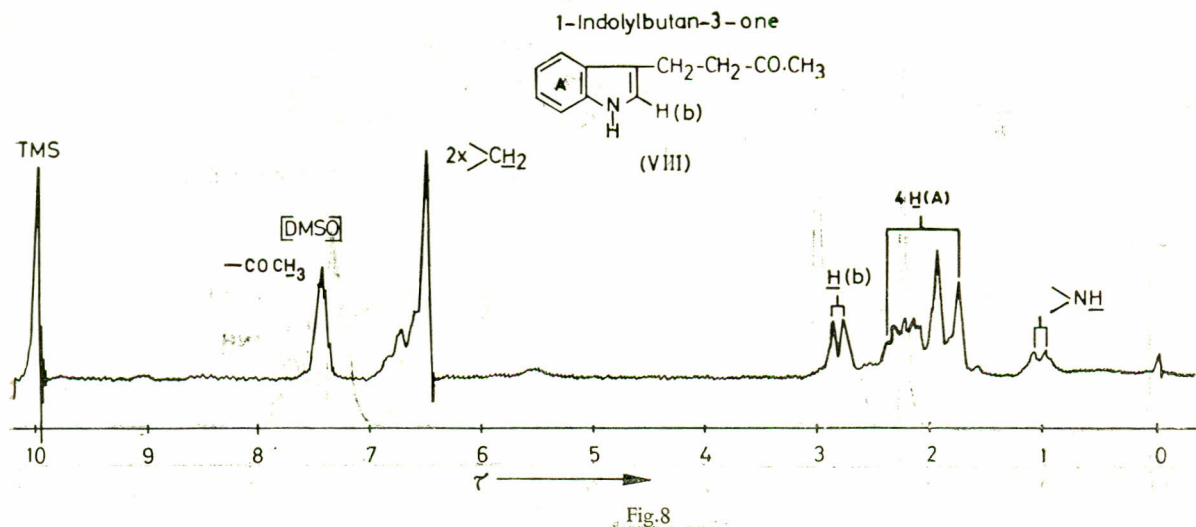
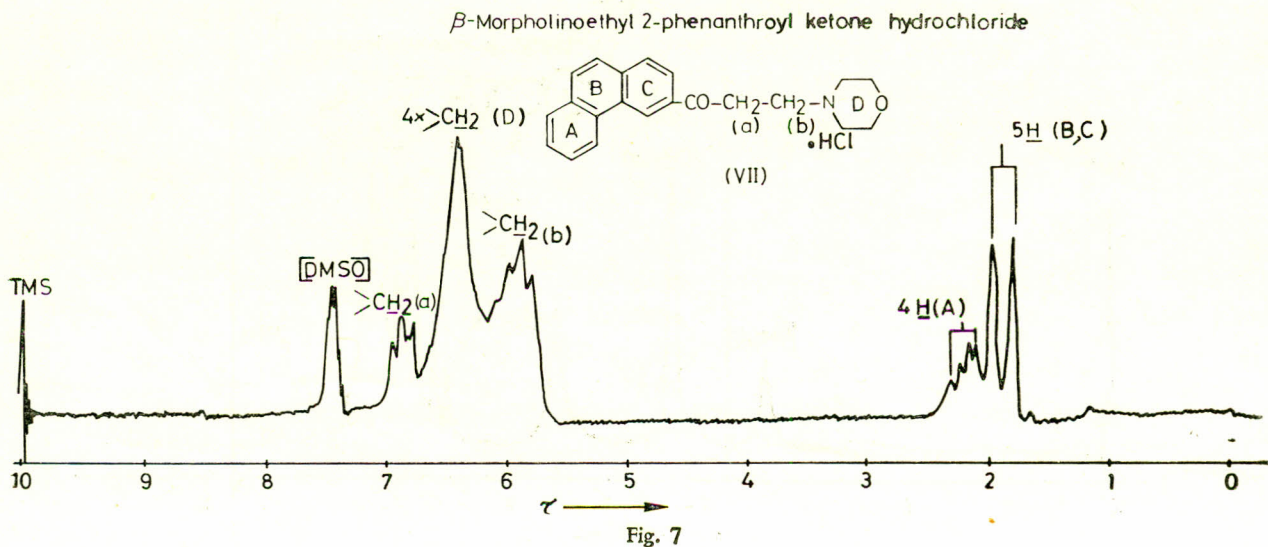


showed an ill-defined doublet centred at τ 2.9 (1H; 7 Hz). The protons of the phenanthrene nucleus appeared as a multiplet centred at τ 2.8 (9H). The benzenoid protons of indole group appeared as a multiplet centred at τ 2.4 (4H). Finally, the remaining proton of the $>NH$ group appeared at τ 2.25 (1H; 8 Hz) as a doublet.

The PMR spectrum of β -morpholinoethyl 2-phenanthroyl ketone hydrochloride (VII), showed two multiplets centred at τ 6.9 (2H) and τ 5.9 (2H) for two methylene groups (a and b) in different environments (J 7 Hz) in each case. A broad singlet appeared at τ 6.42 (8H) for four methylene groups of morphine moiety. The protons of the phenanthrene ring A showed multiplet centred at τ 2.12 (4H). Finally, protons of rings B and C showed a superimposed doublet centred at τ 1.9 (5H; 8 Hz).

The PMR spectrum of 1-indolybutan-3-one (VIII), showed an ill-defined singlet overlapped with the DMSO peak at τ 7.6 (3H) for the C-methyl of acetyl group. There was a broad singlet centred at τ 6.52 (4H) due to two methylene groups attached to β position of the indole group. The α -proton (b) of the indole ring appeared as a doublet centred at τ 2.82 (1H). The benzenoid protons appeared as multiplets centred at τ 2.1 (4H). Finally, the protons of the $>NH$ group showed a doublet centred at τ 1.02 (1H; 8 Hz).

The above PMR studies of all these compounds have not only proved the structures of these compounds but also showed the coupling constants of protons of the methylene groups present in these compounds. The chemical shift of the protons of the indole nucleus appeared more or less in the same region in all these compounds.



Experimental

All the compounds were run on DP-60 Varian associate NMR machine, 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 each compound was about 11-15%.

Acknowledgement.—Our thanks are due to Dr. S.H. Zaidi and Mr. Mohammad Afroze Khan for running the PMR spectra.

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, M. Afroze Khan and Asaf A. Qureshi, Pakistan J. Sci. Ind. Res., **14**, 6 (1971).
3. A. Kamal, Tahira Begum, M. Afroze Khan and Asaf A. Qureshi, Pakistan J. Sci. Ind. Res., **14**, 11 (1971).
4. A. Kamal, Tahira Begum, M. Afroze Khan and Asaf A. Qureshi, Pakistan J. Sci. Ind. Res. **14**, 15 (1971).