

PROTON MAGNETIC RESONANCE SPECTRA OF SOME 8,8'-SUBSTITUTED-1,1'-BINAPHTHLYLS AND RELATED COMPOUNDS

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Abstract. The PMR spectra of 8, 8'-substituted-1, 1'-binaphthyls and related compounds carrying different functional groups as $-\text{COOH}$, $-\text{COOCH}_3$, $-\text{CH}_2\text{OH}$, $-\text{CH}_3$, $-\text{CH}_2\text{Br}$, $-\text{CH}_2\text{OCH}_3$, $-\text{CH}_2\text{OC}_2\text{H}_5$, $-\text{CH}_2\text{OCOCH}_3$ and >C=O forming a bridge between 8' and 2 carbon atoms, have been studied. An unusual chemical shift of methyl ester group at $\tau 7.30$ in these binaphthyl compounds has been observed. In addition to the unusual chemical shift of the methyl ester group the spectra exhibited also a series of quartet and octet in the region between $\tau 1.5-3.9$. The decreased shielding results in a downfield shift of benzenoid protons depending upon the nature of the substituents in these compounds.

The syntheses of 8,8'-substituted-1,1'-binaphthyls have been reported earlier.¹⁻³ The present communication deals with PMR spectra of the compounds shown in Chart 1.

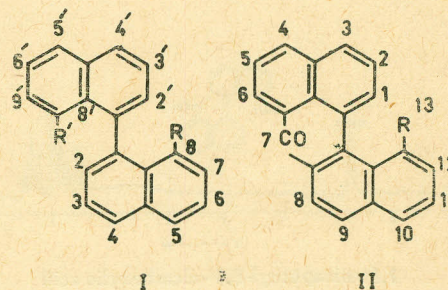
The PMR spectrum of 1,1'-binaphthyl (Ia) in carbon tetrachloride showed a superimposed quartet with *ortho* and *meta* coupling ($J 8$ Hz and 2 Hz) centred at $\tau 2.30$ for the sterically hindered protons H_8, H_8' ; the protons H_2, H_2' appeared as ill-defined quartet at $\tau 2.50$. The protons H_4, H_4' and H_5, H_5' showed a superimposed quartet at $\tau 2.81$ with an *ortho* and *meta* coupling ($J 8$ Hz and 2 Hz). The remaining protons H_3, H_3' ; H_6, H_6' and H_7, H_7' in the molecule showed a multiplet centered at $\tau 2.97$ thus accounting for all the protons in this compound.

The PMR spectrum of 8,8'-dimethyl-1,1'-binaphthyl (Ib) in carbon tetrachloride showed a sharp singlet at $\tau 8.05$ due to two $-\text{CH}_3$ groups situated in an identical environment in 8 and 8' positions. The protons H_2, H_2' and H_7, H_7' appeared at $\tau 2.66$ as a multiplet with *ortho* and *meta* coupling ($J 8$ Hz and 2 Hz); the protons H_4, H_4' and H_5, H_5' appeared as a superimposed quartet at $\tau 3.00$ while the protons H_3, H_3' and H_6, H_6' appeared at $\tau 3.20$. The shielding effect could be explained on the basis of the two $-\text{CH}_3$ groups situated in 8 and 8' positions in the molecule.

The PMR spectrum of 1,1'-binaphthyl-8,8'-dicarboxylic acid (Ic) in dimethyl sulphoxide (DMSO) showed a superimposed quartet centered at $\tau 1.68$ with *ortho* and *meta* coupling ($J 8$ Hz and 2 Hz). The low value of the benzenoid protons H_7 and H_7' was due to the presence of two highly electronegative carboxyl groups oriented in 8 and 8' positions. The protons of the carboxylic hydroxyl group appeared at $\tau 3.44$ as a broad hump and protons H_2, H_2' appeared at $\tau 1.85$ as a quartet. The protons H_4, H_4' ; H_5, H_5' were centered at $\tau 2.20$ and the coupling

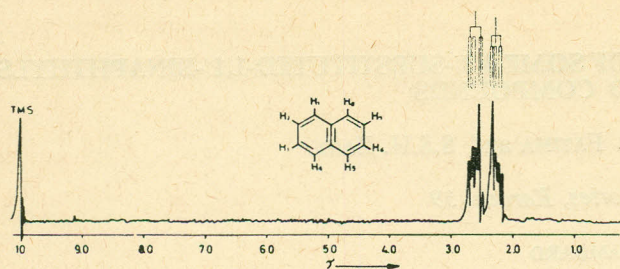
constants were the same as observed in the previous spectra. The decreased shielding resulted in a downfield shift of the benzenoid protons between $\tau 1.30-2.50$ which was accounted for by the presence of the highly electronegative groups.

The PMR spectrum of dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate (Id) in deuteriochloroform showed a sharp singlet at $\tau 7.30$ due to the presence of two $-\text{COOCH}_3$ groups in the molecule. It became difficult to explain the anomalously large shift of these groups in this compound. Normally groups appeared at τ value between 5.80-6.60. This high value

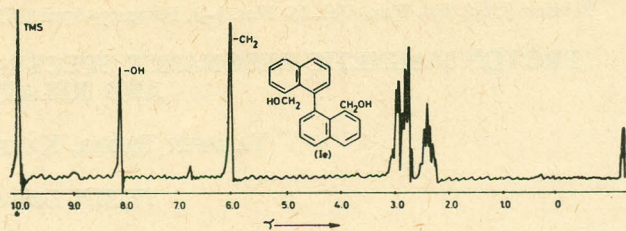


Ia R = $-\text{H}$	R' = $-\text{H}$
Ib R = $-\text{CH}_3$	R' = $-\text{CH}_3$
Ic R = $-\text{COOH}$	R' = $-\text{COOH}$
Id R = $-\text{COOCH}_3$	R' = $-\text{COOCH}_3$
Ie R = $-\text{CH}_2\text{OH}$	R' = $-\text{CH}_2\text{OH}$
If R = $-\text{CH}_2\text{Br}$	R' = $-\text{CH}_2\text{Br}$
Ig R = $-\text{CH}_2\text{OC}_2\text{H}_5$	R' = $-\text{CH}_2\text{OC}_2\text{H}_5$
Ih R = $-\text{CH}_2\text{OCH}_3$	R' = $-\text{CH}_2\text{OCH}_3$
Ii R = $-\text{COOCH}_3$	R' = $-\text{CH}_2\text{O COCH}_3$
Ij R = $-\text{COOCH}_3$	R' = $-\text{CH}_2\text{OH}$
Ik R = $-\text{COOCH}_3$	R' = $-\text{CH}_2\text{Br}$
Il R = $-\text{COOCH}_3$	

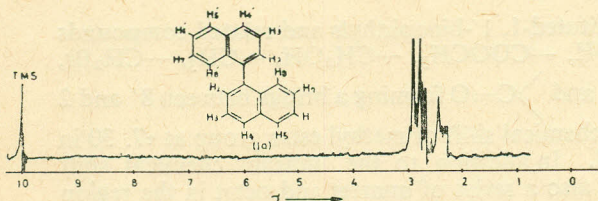
Chart 1.



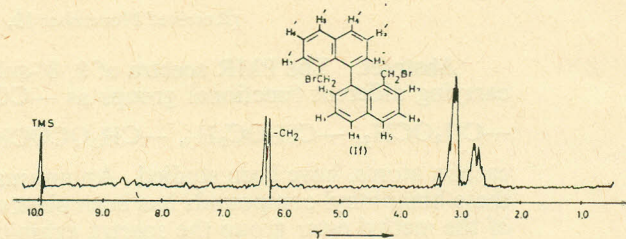
Naphthalene



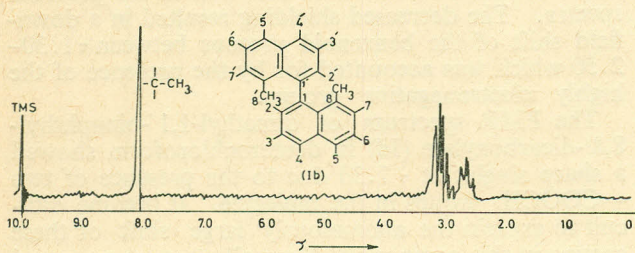
8,8'-Bis(hydroxymethyl)-1,1'-binaphthyl



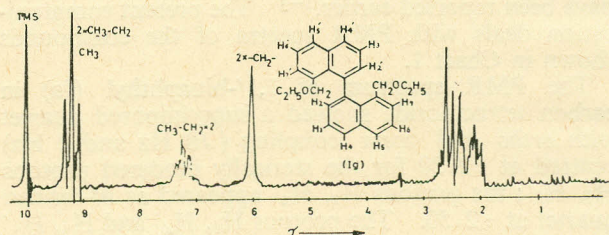
1,1'-Binaphthyl



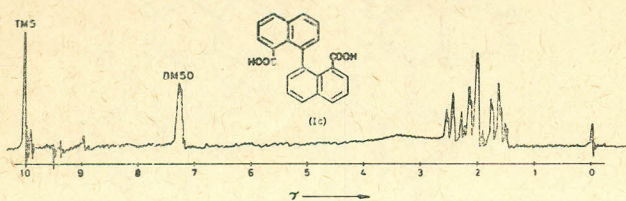
8,8'-Bis(bromomethyl)-1,1'-binaphthyl



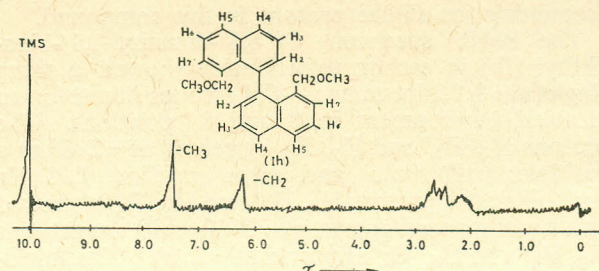
8,8'-Dimethyl-1,1'-binaphthyl



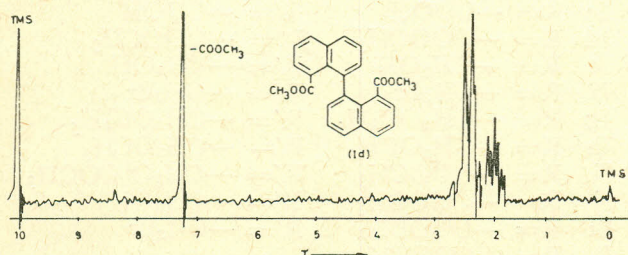
8,8'-Bis(ethoxymethyl)-1,1'-binaphthyl



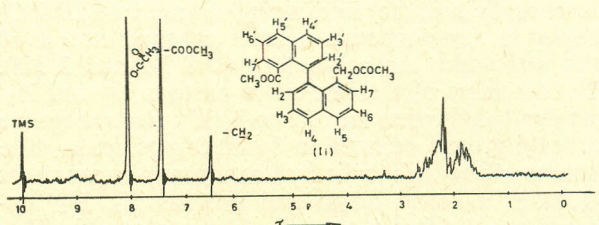
1,1'-Binaphthyl-8,8'-dicarboxylic acid



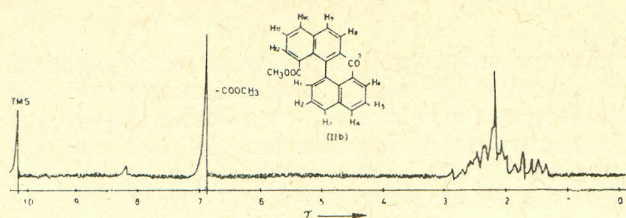
8,8'-Bis(methoxymethyl)-1,1'-binaphthyl



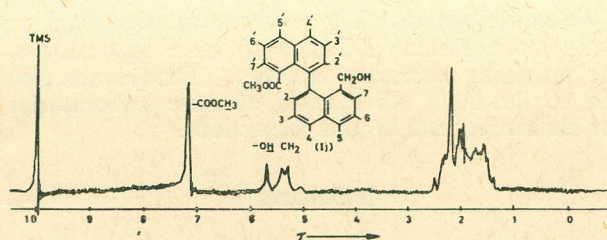
Dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate



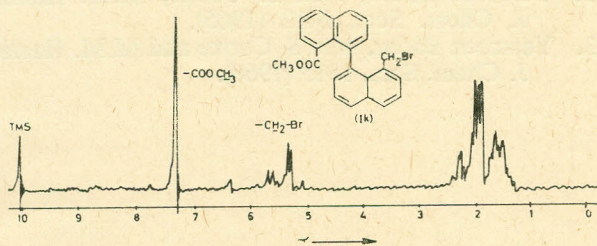
8-Carboxymethyl-8'-acetylmethyl-1,1'-binaphthyl



(Ij)
Methyl-*o* x *o*-dibenzene (anthracene)-13-carboxylate



(Ik)
8-Hydroxymethyl-8'-carboxymethyl-1,1'-binaphthyl



(Il)
8-Bromomethyl-8'-carboxymethyl-1,1'-binaphthyl

could be attributed to the restricted rotation between 1,1'-bond further supported by the low absorption of downward shift of the two protons H_7 and H_7' , which appeared at τ 1.90 as an ill-defined quartet with a coupling constant 8 Hz and 2 Hz. The protons H_2 , H_2' also appeared as a superimposed quartet at τ 2.01 with the same coupling constants as were observed in previous spectra. The protons H_4 , H_4' and H_5 , H_5' appeared as a multiplet at τ 2.54. It was interesting to mention that this particular ester prepared from the corresponding acid with diazomethane yielded two types of crystals, namely needles and plates, on crystallisation from ethanol having different melting points. The PMR spectrum of the needles resolved very nicely in the benzenoid region in spite of the fact that the ester group appeared at the same position.

The PMR spectrum of 8,8'-bis(hydroxymethyl) 1,1'-binaphthyl (Ie) in deuterochloroform showed two singlets at τ 8.12 for the two protons of the hydroxyl groups and τ 6.05 for the two methylene groups attached to the benzene ring. The protons H_7 , H_7' and H_2 , H_2' appeared as an octet at τ 2.35 with *ortho* and *meta* coupling (J 8 Hz and 2 Hz). The protons H_4 , H_5 and H_4' , H_5' appeared as a multiplet at τ 2.90 and the protons H_3 , H_3' and H_6 , H_6' appeared at τ 3.00 thus accounting for all the protons in the molecule.

The PMR spectrum of 8,8'-bisbromomethyl-1,1'-binaphthyl (If) in deuterochloroform appeared as two double doublets centered at τ 6.20 and 6.10 for the two methylene groups situated next to heavy atoms bromine. The benzenoid protons appeared as complex multiplet in the region between τ 2.60 and τ 3.40.

The PMR spectrum of 8,8'-bisethoxymethyl-1,1'-binaphthyl (Ig) in deuterochloroform showed a triplet and a quartet centered at τ 9.07 and τ 7.25 due to A_2B_3 system for the two ethyl groups in the molecule. The methylene protons attached to the benzene ring appeared as a singlet at τ 6.01. The benzenoid protons H_2 , H_2' and H_7 , H_7' centered as a complex multiplet at τ 2.10 and protons H_4 , H_4' and H_5 , H_5' centered at τ 2.30 (J 8 Hz). The remaining protons H_3 , H_6 and H_3' , H_6' appeared as a multiplet at τ 2.59 and in this way all the protons were accounted for.

The PMR spectrum of 8,8'-bismethoxymethyl-1,1'-binaphthyl (Ih) in deuterochloroform appeared as a singlet at τ 7.57 for two $-OCH_3$ groups; the methylene groups attached to benzene ring showed a peak at τ 6.25. The protons H_7 , H_7' and H_2 , H_2' appeared as a multiplet at τ 2.08 and the protons H_4 , H_5 and H_4' , H_5' appeared at τ 2.55 as a quartet with *ortho* and *meta* coupling. The protons H_3 , H_3' and H_6 , H_6' again appeared as a multiplet at τ 2.7 with distinct *ortho* coupling (J 8 Hz).

The PMR spectrum of 8-carboxymethyl,8'-acetoxymethyl-1,1'-binaphthyl (Ii) in carbon tetrachloride showed two sharp singlets appeared at a higher τ value i.e. τ 8.06 for *O*-acetyl, τ 7.45 for the protons of methyl ester while a singlet for methylene group also appeared at τ 6.54. The protons H_7 , H_7' and H_2 , H_2' appeared as a multiplet at τ 1.89 and the protons H_4 , H_4' and H_5 , H_5' appeared as a multiplet centered at τ 2.21. The remaining protons H_3 , H_3' and H_6 , H_6' appeared as a multiplet at τ 2.65.

The PMR spectrum of methyl-7-oxodibenzene anthracene-13-carboxylate (Ij) in deuterochloroform showed a very sharp singlet at τ 6.95 for $-CH_3$ of the ester group. The chemical shift of this group appeared to be very high in comparison to normal methyl ester group. This again could be explained on the basis of the steric hindrance present in the molecule. The benzenoid protons appeared in the region between τ 1.3 to τ 2.9.

The PMR spectrum of 8-carboxymethyl-8'-hydroxymethyl-1,1'-binaphthyl (Ik) in deuterochloroform showed a sharp singlet at τ 7.26 for carboxymethyl ($-COOCH_3$) group and a singlet protons of the benzyl alcohol group appeared as a doublet at τ 5.35 while the benzenoid protons H_2 , H_3 , H_4 , H_5 , H_6 , H_7 and H_2' , H_3' , H_4' , H_5' , H_6' , H_7' appeared as a complex multiplet in the region between τ 1.20 to τ 2.50. The very high value of the $-CH_3$ of the ester group could be again due to the strained ring system present in the molecule.

The above conclusion was further substantiated by the investigation of the spectrum of 8-carboxymethyl 8'-bromomethyl-1,1'-binaphthyl (Il). A sharp singlet appeared at a slightly higher value than the previous compounds for the $-CH_3$ of the ester group

which could be explained on the basis of the presence of 8,8'-substituted-1, 1'-binaphthyl ring system and a relatively stronger electronegative bromine atom instead of a hydroxyl group. The methylene group appeared at τ 5.34. The rest of the benzenoid protons again appeared as a very complex multiplet in the region between τ 2.4 and τ 1.30.

Discussion

It is very interesting to note that due to the steric hindrance in 8,8'-substituted-1,1'-binaphthyl ring system the signal for the *O*-methyl ($O-CH_3$) of the ester group appears significantly at a very high value which has not been reported earlier by any author. The highest value so far observed in other cases is τ 6.60. The reason for this prominently high value for the ester group can be found in the steric hindrance of two binaphthyls ring system in which they are attached at 1,1'- position. It will be very interesting to record the PMR spectrum of dimethyl-2, 2'-binaphthyl-8, 8'-dicarboxylate which should have the normal chemical shift at τ 6.20 for the *O*-methyl of the ester group because the steric hindrance is absent in the system. Further work on these lines is in progress.

Experimental

The compounds under investigation were synthesised as described in earlier communications.^{1,2,3} The PMR spectra were recorded on a Varian DP-60 High Resolution NMR Spectrometer. In each case approximately a 10% (by weight) solution of the compound in deuteriochloroform ($CDCl_3$) or as otherwise stated was used throughout investigations. Tetramethylsilane (TMS) was used as an internal solvent.

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References

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