Proton Magnetic Resonance of Thianaphthenes. II.* The Long-range Coupling between 2- and 6-Hydrogens

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In a previous communication, we have shown the long-range coupling between 3- and 7-hydrogens in some thianaphthenes and have also suggested, from the observation of the line width, the presence of another long-range coupling connected with 2-hydrogen.[1] In this report we will clear up this point. In the spectrum of 5-bromothianaphthene in a 5 mol. % solution in acetone, the signal of the 6-hydrogen consists of eight lines, as is shown in Fig. 1a; therefore, we must consider the coupling between 6-hydrogen and one of the hydrogens in the five-membered ring. The signals of 2- and 3-hydrogens also show second-order splittings by about 0.5 and 0.75 c. p. s. respectively. We have also examined the spectrum of 3,5-dibromothianaphthene in a 1.5 mol. % solution in cyclohexane. In this spectrum, the signal of the 6-hydrogen in question is overlapped with the signal of 2-hydrogen by nearly half, but the other half of it clearly consists of four lines, as was observed in the former compound. On the other hand, the signal of 2-hydrogen is unresolved and broad. Therefore, we can conclude that the 2-hydrogen is coupled to the 6-hydrogen in thianaphthenes. Recently, Black et al. have also suggested the presence of a similar 2,6-coupling in indolizine.[2]

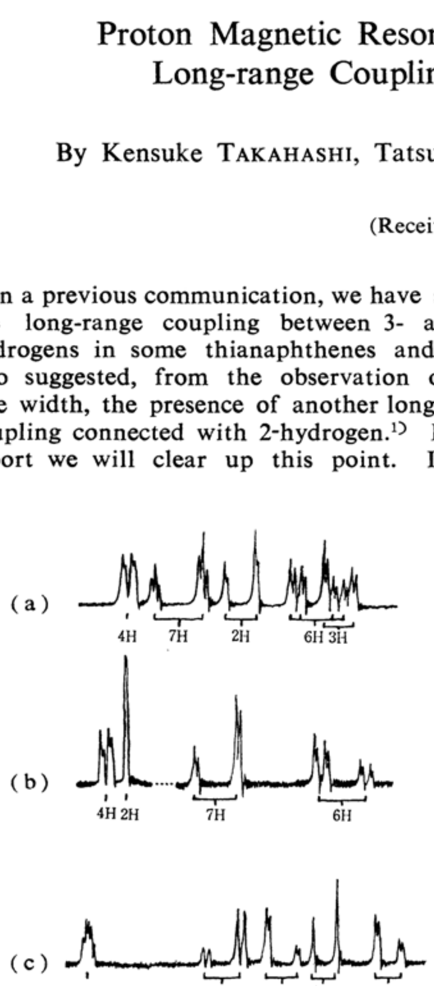

Fig. 1. The ring proton spectra of (a) 5-bromothianaphthene in a 5 mol.% solution in acetone, (b) 3-acetyl-5-bromothianaphthene in a 5 mol.% solution in acetone and (c) 6-carbomethoxythianaphthene in a 3 mol.% solution in carbon tetrachloride. Applied magnetic field increases from left to right in all figures.

It is said that there is a straight zig-zag path or some stereospecificity that gives facilities for coupling to hydrogens.[3] This 2,6- or 3,7-coupling in thianaphthenes is also a typical example in which the interacting hydrogens are located in such a straight zig-zag path as is shown in the following figure by the bold line. Although this kind of zig-zag path is found in some other aromatic compounds,

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* Part II in this series (see Ref. 1 for Part I).

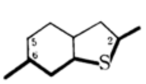
[1] K. Takahashi, T. Kanda and Y. Matsuki, This Bulletin, **37**, 768 (1964).

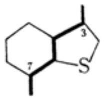
[2] P. J. Black, M. L. Heffernan, L. M. Jackman, Q. N. Porter and G. R. Underwood, *Austr. J. Chem.*, **17**, 1128 (1964).

[3] C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1963); G. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 3886 (1963).

TABLE I. PMR DATA OF SOME THIANAPHTHENE DERIVATIVES, REFERRED TO CYCLOHEXANE AT 60 Mc./sec.

Substituent	Chemical shift, p. p. m.							Coupling, c. p. s.	
	CH_3	2-H	3-H	4-H	5-H	6-H	7-H	J_{37}	J_{26}
5-Br	—	5.93	5.74	6.45	—	5.94	6.21	0.7_5	0.5
3,5-Br_2	—	5.97	—	6.50	—	6.03	6.22	—	0.6
3-CH_3CO, 5-Br	1.10	6.71	—	7.37	—	5.97	6.15	—	0.6
2-CH_3CO, 5-Br	1.15	—	6.30	6.52	—	6.07	6.26	0.7	—
6-$COOCH_3$	2.47	6.13	5.88	6.35	6.54	—	7.13	0.7_5	—
3-Br, 6-$COOCH_3$	2.49	6.12	—	6.36	6.59	—	7.07	—	—
3-Br, 6-$COCH_3$	1.17	6.13	—	6.35	6.50	—	6.94	—	—





such as naphthalene, quinoline, benzofuran, etc., the coupling across the six bonds found here has not yet been reported in these compounds except in *N*-benzylthieno[3,2-b]-pyrrole.4) The 2,5-hydrogens in thianaphthenes are also located in such a position, but no 2,5-coupling has yet been resolved, so any such coupling may be assumed to be smaller than 0.5 c. p. s. if one exists at all. The difference in condition between 2,5- and 2,6-couplings in thianaphthene is mainly due to the presence or absence of the intervening sulfur atom. The sulfur atom seems to play an important role in the transmission of this long-range coupling.

For the verification of our new finding in thianaphthenes, we have also examined some other compounds. The expected 2,6-coupling is also observed in the spectrum of 3-acetyl-5-bromothianaphthene, as Fig. 1b shows. On the other hand, the signal of 6-hydrogen in 2-acetyl-5-bromothianaphthene consists of four lines, as usual. In the spectra of 6-carbomethoxy-, 3-bromo-6-carbomethoxy- and 3-bromo-6-acetylthianaphthenes, no resolved structures were observed in the signals of 2-hydrogens. Table I lists the observed PMR data of our first-order analyses; the observed second-order splitting gives $J_{26} \sim 0.5$ c. p. s. Figure 1 shows some typical spectra of these compounds. The chemical shifts were measured in solutions concentrated 0.1 g./cc. or less in carbon tetrachloride containing 0.5 wt. % cyclohexane as an internal reference.

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4) H. S. Gutowsky and A. L. Porte, *J. Chem. Phys.*, 35, 839 (1961).