Long-range Proton Spin-Spin Interactions in Thianaphthenes

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The long-range coupling between the protons in different aromatic rings has been observed recently by several authors in quinoline,⁽¹⁾ in *N*-benzylthieno [3, 2-b] -pyrrole,⁽²⁾ in indene,⁽³,⁴⁾ in benzofuran⁽⁴⁾ and in acridine.⁽⁵⁾ In this report we will present the results observed in the long-range coupling between the 3- and 7-hydrogens in some thianaphthenes. In the spectrum of thianaphthene itself, this coupling is difficult to obtain directly from the signals in a carbon tetrachloride, cyclohexane or acetone solution because of the overlapping of the signals, but in the spectra of some methylthianaphthenes it may be observed directly and with certainty. In the spectrum of 2-methylthianaphthene in a carbon tetrachloride solution, the signal of the 3-hydrogen appears at 5.40 p. p. m. with reference to cyclohexane and shows a quintet-like structure. This means that the 3-hydrogen is coupled to the 2-methyl hydrogens and to one of the other hydrogens. In the spectrum of 3-methylthianaphthene, the signal of the 2-hydrogen appears at 5.51 p. p. m. and shows a quartet-like structure, showing the expected coupling with the 3-methyl hydrogens only. In the spectrum of 5- or 6-methylthianaphthene, the signals of the 2- and 3-hydrogens appear as a doublet and as a double doublet respectively. A typical spectrum in the aromatic region of 5-methylthianaphthene is shown in Fig. 1. In the spectrum of 4-methylthianaphthene, the signals of the 2- and the 3-hydrogens look like a singlet in a carbon tetrachloride or cyclehexane solution because of nearly the same chemical shift between the two hydrogens, whereas those in an acetone solution appear as a doublet and as a double doublet, like those observed in 5- or 6-methylthianaphthene.

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TABLE I. PMR DATA OF METHYLTHIANAPHENES, 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}
2-CH_3	1.09	—	5.40	~6.1	~5.7	~5.7	~6.1	1.0~0.5
3-CH_3	0.96	5.51	—	~6.2	~5.8	~5.8	~6.2	—
4-CH_3	1.14	5.86	5.86	—	5.59	5.73	6.19	0.7_5
5-CH_3	0.99	5.83	5.67	6.04	—	5.60	6.20	0.7_5
6-CH_3	1.00	5.78	5.73	6.16	5.63	—	6.14	0.7_5
7-CH_3	1.10	5.85*	5.80*	6.12	5.75	5.57	—	—

* Assignment uncertain

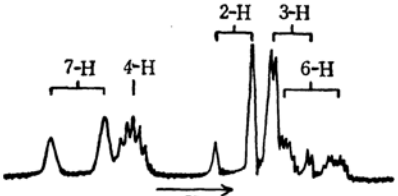

Fig. 1. The ring proton spectrum of 5-methylthianaphthene, in the 5 mole % solution in cyclohexane at 60 Mc./sec.

In the spectrum of 7-methylthianaphthene, the signals of the 2- and 3-hydrogens in a carbon tetrachloride or cyclehexane solution look like a singlet, but those in an acetone solution appear as two doublets, showing no resolved second-order splitting. These facts clearly show that the 3-hydrogen is coupled to the 7-hydrogen in thianaphthenes. The observed second-order splitting gives J_{37}~0.7 c. p. s. in each case.

Another fact of interest has been also observed in the spectrum of 7-methylthianaphthene in an acetone solution. Two doublets originating from the 2- and 3-hydrogens in this compound have different line widths. The one at the lower field is somewhat broader than the other. This suggests the presence of another long-range coupling in this system, for example, one between the 2- and 4-hydrogens, but the assignment is still in question at present.

Table I lists the observed PMR data of our first-order analyses. The chemical shifts were measured in about 0.1 g./cc. solutions in carbon tetrachloride containing 0.5 wt. % cyclohexane as an internal reference.

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