SHORT COMMUNICATIONS

The Proton Magnetic Resonance of Thianaphthenes. III.* The Long-range Coupling Observed in Side-chain Methyl Hydrogens in Some Methylthianaphthenes

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In this report we will discuss the coupling observed in methyl hydrogens in some methylthianaphthenes. The signal of the methyl hydrogens in 2- or 3-methylthianaphthene splits into a doublet with a splitting of about 1 c. p. s. as a result of its coupling with an adjacent ring hydrogen. However, the signal of methyl hydrogens in 4-, 5-, 6- or 7-methylthianaphthene shows a more complex structure than the doublet observed in 2- or 3-methylthianaphthene. This means that there exists some coupling between methyl hydrogens and their non-adjacent ring hydrogens in addition to the

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* See Refs. 1 and 2 for Parts I and II.

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

2) K. Takahashi, T. Kanda, F. Shoji and Y. Matsuki, ibid., 38, 508 (1965).

TABLE I. PMR DATA OF SOME THIANAPHTHENE DERIVATIVES IN CARBON TETRACHLORIDE, REFERRED TO CYCLOHEXANE AT 60 Mc./sec. Parenthesis shows the chemical shift of the substituent.

Substituent	Chemical shift p. p. m.						Coupling c. p. s.
	2-H	3-H	4-H	5-H	6-H	7-H	J_{23}
5-Br[2]	5.93	5.74	6.45	—	5.94	6.21	5.6
6-COOCH$_3$[2]	6.13	5.88	6.35	6.54	(2.47)	7.13	5.4
2-CH$_3$[1]	(1.09)	5.40	~6.1	~5.7	~5.7	~6.1	1.1
3-CH$_3$[1]	5.51	(0.96)	~6.2	~5.8	~5.8	~6.2	1.0_5
2,3-(CH$_3$)$_2$	(1.00)	(0.80)	~6.1	~5.8	~5.8	~6.1	0.7_5
2,3-(CH$_3$)$_2$, 6-COCH$_3$	(1.05)	(0.83)	6.00	6.35	(1.10)	6.77	0.7

Fig. 1. The PMR spectrum of 2,3-dimethylthianaphthene in the 5.2 mol. % solution in carbon tetrachloride at 60 Mc./sec. Applied magnetic field increasing from left to right.

coupling between the methyl hydrogens and their adjacent ring hydrogens. Similar results have already been presented for some other aromatics.[3] In the spectrum of 2,3-dimethylthianaphthene, two methyl signals, at 0.80 and 1.00 p. p. m. with reference to cyclohexane, corresponding to 3-methyl and 2-methyl hydrogens respectively, have quartet structures, as is shown on the right side of Fig. 1. The magnitude of these splittings is about 0.7 c. p. s. This may be attributed to the coupling between two methyl hydrogens in 2,3-dimethylthianaphthene. The present results give us some information about the mechanism of the side-chain coupling in methylthianaphthenes and indicate that it is similar to that in methylthiophenes.[4]

Hoffman described the methyl substitution technique used to check the mechanism of coupling.[5] Some compounds were taken up in order to compare the coupling of J_{23} in thianaphthenes. Table I lists the observed PMR data of the first-order analyses. $J_{2\text{-H},\,3\text{-H}}$ is about 5 c. p. s. in thianaphthenes. When we substitute a methyl group for a 2- or 3-positioned ring hydrogen, a $J_{2\text{-CH}_3,\,3\text{-H}}$ or $J_{2\text{-H},\,3\text{-CH}_3}$ value of about 1 c. p. s. is observed, showing a great decrease as compared with $J_{2\text{-H},\,3\text{-H}}$. After the further substitution of a methyl group for the remaining 2- or 3-positioned ring hydrogen, we get a $J_{2\text{-CH}_3,\,3\text{-CH}_3}$ value of about 0.7 c. p. s., which has the same order of magnitude as $J_{2\text{-H},\,3\text{-CH}_3}$ or $J_{2\text{-CH}_3,\,3\text{-H}}$. This leads to the conclusion that the side-chain coupling in methylthianaphthenes is mainly due to the π-electron contact contribution.

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3) R. A. Hoffman and S. Gronowitz, *Arkiv. Kemi*, **16**, 563 (1960); K. Takahashi, Y. Matsuki, Y. Miyake and G. Hazato, This Bulletin, **34**, 1599 (1961); G. P. Newsoroff and S. Sternhell, *Tetrahedron Letters*, **1964**, 3499.

4) S. Gronowitz, Bo Gestblom and R. A. Hoffman, *Acta Chem. Scand.*, **15**, 1201 (1961).

5) R. A. Hoffman and S. Gronowitz, *Arkiv. Kemi*, **16**, 471 (1960).