The Proton Magnetic Resonance of Thianaphthenes. IV. The Estimation of the Chemical Shifts of Thianaphthene by Partial Deuteration

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In our previous communications[1-3] we have discussed some long-range coupling constants observed in thianaphthenes. The spectrum of thianaphthene itself is too complex to analyze. Therefore we tried to prepare the 5-, 6- and 7-deuterothianaphthenes and to analyze their proton spectra. Deuteration was done by the reduction of the corresponding bromothianaphthenes. The reduction was carried out by zinc and deuterated acetic acid. Details of the preparation will be published later somewhere. The spectra of the deuterated products are shown in Fig. 1. Spectra were taken in 5 mole per cent solutions in carbon tetrachloride, in cyclohexane and in acetone, with a small amount of tetramethylsilane as an internal reference. The first-order analyses are possible in the cases of 5- and 6-deuterothianaphthenes but not in the case of 7-deuterothianaphthene. The spectrum of 7-deuterothianaphthene is an ABX type which is very close to AA′X type. The results of the chemical shifts obtained are shown in Table I. Agreement of the chemical shifts given for three deuterated compounds is good enough to estimate the chemical shifts of thianaphthene, as is shown in the lowest line in Table I. A characteristic point of thianaphthene is that the chemical shifts of the 5- and the 6-hydrogens are almost the same but the former seems to be a little larger than the latter. The difference of the chemical shifts of about 0.5 p. p. m. between the 4- and 5- or between the 6- and 7-hydrogens will be explained by the ring current effect similar to that of natpthalene but it is somewhat larger than that of naphthalene.[4] Therefore the whole part of the difference can not be explained by only the ring current effect. The chemical shift of the 7-hydrogen is larger than that of the 4-hydrogen. This may be due to the magnetic anisotropy or electronic effect of the sulfur atom. Approximate values of the coupling constants between ring hydrogens for deuterothianaphthenes are following: $J_{23}=5._5$, $J_{26}=0.5$, $J_{37}=0.7_5$, $J_{45}=J_{67}=8._0$—$7._5$, $J_{56}=7._5$—$7._0$, $J_{46}=J_{57}=1._5$—$1._0$, $J_{47}=0.7$ c. p. s. respectively. Some of the coupling constants were determined only approximately because of the broadness of the lines caused by the interaction with the deuterium.

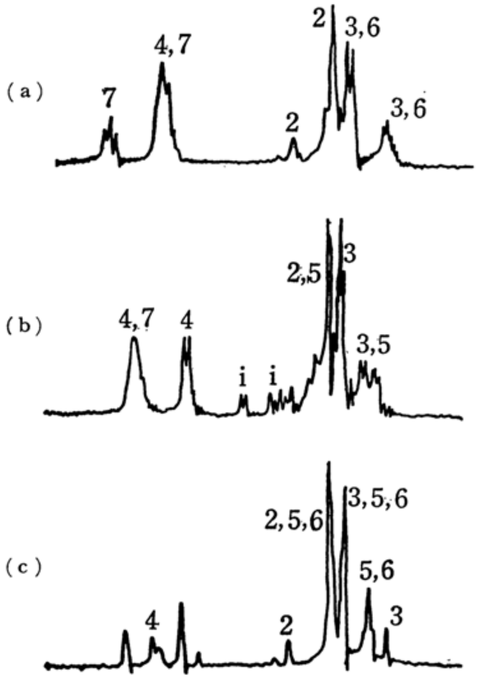

Fig. 1. The PMR spectra of some deuterated thianaphthenes in carbon tetrachloride at 60 Mc.p.s. Applied magnetic field increases from left to right and the number on each peak shows the assignment.
(a) 5-Deuterothianaphthene,
(b) 6-Deuterothianaphthene,
(c) 7-Deuterothianaphthene

TABLE I. CHEMICAL SHIFTS OF SOME THIANAPHTHENE DERIVATIVES IN CARBON TETRACHLORIDE, REFERRED TO TMS AT 60 Mc.p.s.

Substituent	Assignment					
	2-H	3-H	4-H	5-H	6-H	7-H
5-D	7.33	7.23	7.72_5	—	7.24	7.78_5
6-D	7.34_5	7.21_5	7.72_5	7.25	—	7.79
7-D	7.30_5	7.22_5	7.71	7.26	7.23	—
— (Estimated)	7.33	7.22	7.72	7.26	7.24	7.79

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[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).

[3] K. Takahashi, T. Kanda and Y. Matsuki, This Bulletin, **38**, 1799 (1965).

[4] N. Jonathan, S. Gordon and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962); B. P. Dailey, ibid., **41**, 2304 (1964).