Proton Magnetic Resonance Spectra of Methylthiophenesulfonylchlorides

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In the previous communication[1], the relative magnitude of the coupling constants for the ring protons in thiophene derivatives was assumed to be $J_{23}>J_{34}>J_{25}>J_{24}$, in which the values for J_{25} and J_{24} could not be determined experimentally. This assumption is in accordance with the recent experimental works by Gronowitz and Hoffman[2]. In this note, the experimental results of the proton magnetic resonance spectra for the six isomers of methylthiophenesulfonylchloride are presented. Those results complement the previous communication on the substituted thiophenes. The observed values of J_{25} and J_{24} and some experimental coupling constants for the methyl group and the ring proton are also presented. Some qualitative results of the solvent effect on the chemical shifts of these isomers are also presented.

Experimental

The apparatus and procedure were similar to those previously described[1], and cyclohexane was used as an internal reference. The compounds used in the present observations were synthesized by Matsuki and his collaborators. Details of the preparation of these new compounds will be given later in Journal of the Chemical Society of Japan, Ind. Chem. Sec. The boiling points and the measured conditions of the samples are given in Table I; with respect to these six isomers, 2-methyl-5-thiophenesulfonylchloride is the only one which is reported in the literature[3], as far as we know.

TABLE I

Substituent	B. p. °C/mmHg	Measured condition wt. % Sample	CCl_4	C_6H_{12}
2-CH_3, 3-SO_2Cl	91~93/3	77.9		22.1
2-CH_3, 4-SO_2Cl	92~94/3	56.9	30.7	12.4
2-CH_3, 5-SO_2Cl	96~98/3	81.9		18.1
3-CH_3, 2-SO_2Cl	98~100/2.5	83.2		16.8
3-CH_3, 4-SO_2Cl	96.2~97/3	82.7		17.3
3-CH_3, 5-SO_2Cl	100~101/3	78.9		21.1

Results and Discussion

The chemical shifts for the ring protons and for the methyl protons are given in Table II, in c. p. s. at 40 Mc./sec. The values given here are reproducible within the deviation of about 1 c.p.s. Each of the two substituents, methyl and chlorosulfonyl groups, as previously

TABLE II. THE PROTON MAGNETIC RESONANCE DATA IN METHYLTHIOPHENESULFONYLCHLORIDES, REFERRED TO CYCLOHEXANE IN C. P. S. AT 40 Mc./sec.

Substituent	Assignment 2-H	3-H	4-H	5-H	CH_3
2-CH_3, 3-SO_2Cl	—	—	234	226	52
2-CH_3, 4-SO_2Cl	—	226	—	257	44
2-CH_3, 5-SO_2Cl	—	216	247	—	46
3-CH_3, 2-SO_2Cl	—	—	223	250	47
3-CH_3, 4-SO_2Cl	228	—	—	270	44
3-CH_3, 5-SO_2Cl	239	—	247	—	36

1) K. Takahashi, Y. Matsuki, T. Mashiko and G. Hazato, This Bulletin, **32**, 156 (1959).

2) S. Gronowitz and R. A. Hoffman, (a) *Arkiv för Kemi*, **13**, 279 (1958); (b) ibid., **15**, 45 (1959); (c) ibid., **16**, 501 (1960); (d) ibid., **16**, 515 (1960); (e) idid., **16**, 539 (1960); (f) ibid., **16**, 563 (1960); (g) *Acta Chem. Scand.*, **13**, 1687 (1959).

3) W. E. Truce and M. F. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951).

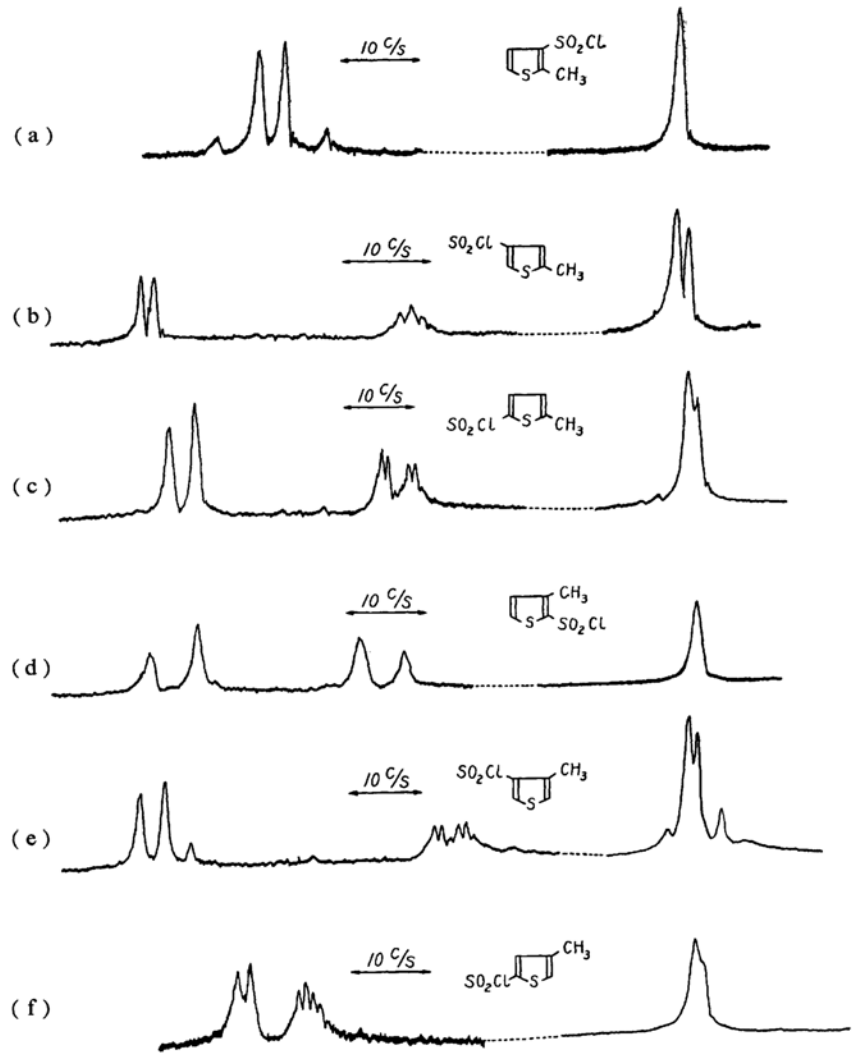

Fig. 1. The proton magnetic resonance spectra at 40 Mc./sec., showing
(a) 2-methyl-3-thiophenesulfonylchloride
(b) 2-methyl-4-thiophenesulfonylchloride
(c) 2-methyl-5-thiophenesulfonylchloride
(d) 3-methyl-2-thiophenesulfonylchloride
(e) 3-methyl-4-thiophenesulfonylchloride
(f) 3-methyl-5-thiophenesulfonylchloride.
Applied magnetic field increases from left to right in all figures. Some extra peaks probably due to the presence of the small isomeric impurities are observed in c, e and f.

reported[1], gives the reverse effect on the chemical shift, so that all spectra here observed can be assigned easily from the standpoint of the chemical shift. In a case where the signal is split by the indirect spin-spin interaction, the shift given in Table II is that for the center of the resonance pattern, so that the difference of the values given for two ring protons in a compound (for example, in 2-methyl-3-thiophenesulfonylchloride, 234 minus 226 equals to 8 c.p.s.) does not equal the true chemical shift for those ring protons, but equals $(J^2+\delta^2)^{1/2}$. The analysis of the two-proton system was reported very early by Hahn and Maxwell[4], and later by Bannerjee, Das and Saha[5]. In this system, the spectrum consists of two

4) E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).
5) M. K. Bannerjee, T. P. Das and A. K. Saha, *Proc. Roy. Soc.*, **A226**, 490 (1954).

doublets; the separation in each doublet just gives the coupling constant between two protons. The disubstituted thiophenes are also the typical model of the two-proton system in which the analysis of the spectrum can be done very easily. But sometimes, as in the case of some methylthiophenesulfonylchlorides, the spectra are somewhat complicated owing to the small interaction between the ring protons and the substituents. The magnitude of the coupling constant for the ring proton and its neighboring methyl protons, as previously reported[1], has the order of about 1.0 c.p.s.; however, the chemical shift between them is more than 170 c.p.s. at 40 Mc./sec. The chemical shifts are here so large compared with the coupling constants (J/δ <0.006) that the spectra can be analyzed by the simple method of the two-proton system. The results of the simple treatment are given in Table III.

TABLE III. THE COUPLING CONSTANTS (J) AND THE CHEMICAL SHIFTS (δ) OF TWO RING PROTONS IN METHYLTHIOPHENESULFONYLCHLORIDES IN c. p. s. AT 40 Mc./sec. MEASURED CONDITIONS ARE SUMMARIZED IN TABLE I

Substituent	J	δ
2-CH_3, 3-SO_2Cl	5.3±0.1	6.6±0.1
2-CH_3, 4-SO_2Cl	1.5±0.1	29.5±0.6
2-CH_3, 5-SO_2Cl	4.1±0.1	30.6±0.1
3-CH_3, 2-SO_2Cl	5.2±0.1	26.2±0.1
3-CH_3, 4-SO_2Cl	3.5±0.1	40.2±0.3
3-CH_3, 5-SO_2Cl	1.8±0.1	7.5±0.1

The proton magnetic resonance spectra of the six isomers studied are reproduced in Fig. 1, in which the ring proton spectra are shown at the left-hand side and the methyl proton spectra at the right-hand side. With respect to the ring proton spectra, a and d in Fig. 1 show the typical type of two-proton system; on the other hand, the other figures in Fig. 1 show some small splittings caused by methyl protons. For 2-methyl-3-thiophenesulfonylchloride, each of the two ring proton spectra is a little asymmetric as shown in a of Fig. 1. The doublet at the low field side is somewhat broader than the doublet at the high field side. Similar broadening is observed also in the doublet at the high field side, the 4-proton spectrum in 3-methy-2-thiophenesulfonylchloride, as shown in d of Fig. 1. For 2-methyl-4-, 2-methyl-5-, 3-methyl-4- and 3-methyl-5-thiophenesulfonylchloride, as shown in b, c, e and f in Fig. 1*, the ring proton spectra consist of two doublets. The one at the low field side has a simple structure and the other doublet at the high field side shows the fine structure caused by the interaction with methyl protons. The methyl proton spectra at the higher field side show also a doublet. In these four isomers, the 2-methyl group couples to 3-proton with a coupling constant of 1.1 c. p. s. However, the 3-methyl group couples to 2-proton with the same value but does not couple to 4-proton with the same order of coupling constant. This trend was also obseved in the spectrum of 3-methyl-2-thiophenesulfonylchloride, as shown in d of Fig. 1., in which no resolved fine structure was observed. The interaction between 4-proton and the adjacent methyl group is small. But the spectra of 4-proton are somewhat broader than those of 5-proton in 2-methyl-3- and 3-methyl-2-thiophenesulfonylchloride, as shown in a and d of Fig. 1. Consequently, it can be assumed that 2-methyl or 3-methyl group couples to 4-proton with a small coupling constant but couples to 5-proton with no appreciable constant. Similar results on the long range coupling in thiophene derivatives also have been obtained by others[2f,2g,6].

The coupling constants between two ring protons in the six isomers studied are 5.3 and 5.2 c.p.s. for J_{23}, 4.1 c.p.s. for J_{34}, 3.5 c.p.s. for J_{25}, and, 1.5 and 1.8 c.p.s. for J_{24}, as shown in Table III. The previous assumption[1] that the coupling constants between the ring protons for thiophene derivatives are $J_{23} > J_{34} > J_{25} > J_{24}$, is also consistent with the present observed values. It is very interesting to note that the observed coupling constant between the two protons by way of the sulfur atom (J_{25}) are relatively large, as compared with the meta-coupling constants for the benzene derivatives[7]; this trend is also obtained in thiophene which was analyzed recently by several authors[2b,8,9].

Chemical shifts depend upon the nature and the concentration of the solvents, so that the observation of the solvent effects on the chemical shift in the present compounds has also been made. The measured conditions and the results are summarized in Table IV. Three typical solvents were used, cyclohexane and carbon tetrachloride as nonpolar solvents, and acetone as a polar solvent. The experiment was carried out with the definite dilute solution of the compounds in each solvent, because of the limited amount of the synthesized material

* In c, e and f in Fig. 1, some extra peaks probably due to the presence of small isomeric impurities are observed.

6) P. L. Corio and I. Weinberg, *J. Chem. Phys.*, **31**, 569 (1959).
7) H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957).
8) T. Isobe, *Bull.Chem. Res. Inst. Non-Aqueous Solutions, Tohoku Univ.*, **9**, 115 (1960).
9) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 2095 (1959).

TABLE IV. DISPLACEMENTS OF THE PROTON RESONANCES WHEN THE SAMPLES ARE DILUTED WITH CYCLOHEXANE, CARBON TETRACHLORIDE AND ACETONE, IN C. P. S. AT 40 MC./SEC., REFERRED TO THE VALUES GIVEN IN TABLE II, MINUS SIGN SHOWING THE DISPLACEMENT TO THE HIGHER FIELD

Substituent	Measured Solution, wt. %				Displacement, c. p. s.				
	Sample	C_6H_{12}	CCl_4	$(CH_3)_2CO$	2-H	3-H	4-H	5-H	CH_3
2-CH_2, 3-SO_2Cl	10.6	89.4			—	—	−1.5	−6.5	−0.5
2-CH_3, 4-SO_2Cl	10.6	83.7	5.7		—	−2.0	—	−5.5	−2.5
2-CH_3, 5-SO_2Cl	8.0	92.0			—	−8.0	−6.0	—	−3.5
3-CH_3, 2-SO_2Cl	11.5	88.5			—	—	−7.5	−10.0	−2.0
3-CH_3, 4-SO_2Cl	12.4	87.6			−8.5	—	—	−7.5	−1.5
3-CH_3, 5-SO_2Cl	11.3	88.7			−9.0	—	−5.0	—	−2.5
2-CH_3, 3-SO_2Cl	6.7	1.9	91.4		—	—	+1.0	−1.5	+2.5
2-CH_3, 4-SO_2Cl	5.0	1.1	93.9		—	0.0	—	−1.5	+1.0
2-CH_3, 5-SO_2Cl	4.4	1.0	94.6		—	−3.0	−1.5	—	+0.5
3-CH_3, 2-SO_2Cl	6.4	1.3	92.3		—	—	−4.0	−5.0	0.0
3-CH_3, 4-SO_2Cl	7.2	3.7	89.2		−5.0	—	—	−3.5	0.0
3-CH_3, 5-SO_2Cl	8.2	2.2	89.6		−3.5	—	−1.5	—	+1.0
2-CH_3, 3-SO_2Cl	14.6	15.4		70.0	—	—	+4.5	+13.5	+3.0
2-CH_3, 4-SO_2Cl	9.1	13.6	5.0	72.3	—	+7.5	—	+16.0	+2.5
2-CH_3, 5-SO_2Cl	12.8	14.5		72.7	—	+8.0	+8.0	—	+4.0
3-CH_3, 2-SO_2Cl	13.2	14.3		72.5	—	—	+7.5	+14.5	+1.5
3-CH_3, 4-SO_2Cl	15.3	14.4		70.3	+13.0	—	—	+12.0	+0.5
3-CH_3, 5-SO_2Cl	14.0	15.1		70.9	+16.0	—	+8.0	—	+2.0

at hand, and a small amount of cyclohexane was used also as an internal reference. One of our aims in this experiment was to find a key for the assignment of the chemical structure by the NMR spectrum. As shown in Table IV, it is clear that, in the six compounds studied, all α-protons are sensitive to the polarity of the solvents as compared with β-protons, notably in the case of the solution in acetone. It should be kept in mind that the self-polarizabilities given by de Heer[10] for α- and β-carbon atoms in thiophene are qualitatively in agreement with the present results of the solvent effect.

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10) J. de Heer, *J. Am. Chem. Soc.*, 76, 4802 (1954).