Proton Magnetic Resonance Spectra of Some Thenyl Derivatives[1]

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(Received May 29, 1962)

In the previous works[2,3], we investigated the proton magnetic resonance spectra of some thiophene derivatives. In these studies, the coupling constants and the chemical shifts were measured and discussed in connection with their structures. In the present case we have extended our investigation to some thenyl derivatives.

Experimental

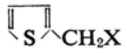
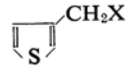
The procedure and apparatus were similar to those described previously[2]. All spectra were observed with a Varian high resolution NMR spectrometer at 40 Mc. The chemical shifts were read directly from the spectra recorded with a Sanborn model 127 recorder. Sweep rate of the magnetic field was calibrated frequently by measuring the displacement between the two peaks for benzene-cyclohexane mixture (1 : 1 by volume). The value assumed for this displacement in the present work is 227 c.p.s. at 40 Mc.[4], although more recent measurements indicate that this value is about 230 c.p.s. at 40 Mc.[5] The small sweep rate was calibrated by running acetaldehyde, with its known splitting of 2.85 c.p.s. The spectra of most of the compounds were measured in cyclohexane solutions and chemical shifts referred to cyclohexane were read in c.p.s., carbon tetrachloride, carbon disulfide, trichloroethylene and acetone were used as solvents in some cases.

All thenyl derivatives and some of the corresponding benzyl derivatives used in the present observations were prepared by the usual method with exception of the commercially available products. The measured conditions and the boiling points or the melting points of the compounds studied are given in Table I.

Results and Discussion

Tables II, III and IV list the results of the chemical shifts and the coupling constants

TABLE I

	Compound	B. p. °C/mmHg	Ref.	Measured condition, wt.%		
				Sample	C_6H_{12}	Solvent
						
	CH_3	133∼135	a	80.8	19.2	
	CN	115∼120/22	b	79.8	20.2	
	NH_2	81∼83/17	c	80.8	19.2	
	C_6H_5	87/8	d	89.3	10.7	
	SCN	105∼110/3	7	79.5	20.5	
X =	C_4H_3S	125∼129/9	e	14.9	4.3	80.8 (CCl_4)
	OCH_3	63∼64/17	f	85.4	14.6	
	Br*	80∼85/15	6	80.6	19.4	
	Cl	73∼75/17	e	83.0	17.0	
	OH	94∼96/12	c	80.6	19.4	
	OAc	92∼94.5/11	g	80.5	19.5	
						
	SCN	109∼111/3	7	88.0	12.0	
	OCH_3**	65∼67/17	h	48.4	7.0	44.6 (CCl_4)
X =	Br**	63∼80/3	i	83.2	16.8	
	CN**	115∼120/17	i	83.1	16.9	
	COOH	m. p. 79∼80	i	11.2	1.7	87.1 (C_2HCl_3)

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[1] Presented partly at the Meeting of Tohoku District of the Chemical Society of Japan, Yonezawa, October, 1961.

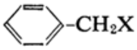
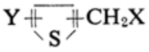
[2] K. Takahashi, Y. Matsuki, T. Mashiko and G. Hazato, This Bulletin, 32, 156 (1959).

[3] K. Takahashi, Y. Matsuki, Y. Miyake and G. Hazato, ibid., 34, 1599 (1961).

[4] B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, 77, 3977 (1955).

[5] a) B. L. Corio and B. P. Dailey, ibid., 78, 3043 (1956); b) C. M. Huggins and D. R. Carpenter, *J. Phys. Chem.*, 63, 238 (1959).

TABLE I (Continued)

Compound			B. p. °C/mmHg	Ref.	Measured condition, wt.%		
					Sample	C_6H_{12}	Solvent
							
X =	CH_3			j	91.9	8.1	
	CN		116∼117/20	k	81.1	18.9	
	COOH		m. p. 76	l	16.5	4.0	79.5 (C_2HCl_3)
	NH_2			j	83.0	17.0	
	C_6H_5			j	92.5	7.5	
	SCN		102∼103/7	h	79.4	20.6	
	OCH_3			j	82.7	17.3	
	Br			j	82.6	17.4	
	Cl			j	82.0	18.0	
	OH			j	83.0	17.0	
	OAc			j	79.4	20.6	
							
	X	Y					
	2-CN	5-I	m. p. 58∼58.5	h	10.3	1.7	88.0 (CCl_4)
	2-SCN	3-NO_2	m. p. 109∼110	h	18.3	10.6	71.1 ($(CH_3)_2CO$)
	2-SCN	5-CH_2SCN	m. p. 74∼75	7	1.5	0.9	97.6 (CS_2)
	2-SCN	5-NO_2	m. p. 44.5∼45	m	95.7	4.3	
	3-SCN	2-NO_2	m. p. 76	h	7.4	15.5	77.1 ($(CH_3)_2CO$)
	2-OCH_3	5-Br	91∼92/10	f	86.3	13.7	
	2-Br	3-NO_2	m. p. 60∼61	n	22.0	4.7	73.3 (CCl_4)
	2-Br	5-Br	84∼86/2	6	84.6	15.4	
	3-Br	2-NO_2	m. p. 67	n	7.1	1.4	91.5 (CCl_4)
	2-Cl	5-Cl	92∼94/15	h	83.6	16.4	
	2-Cl	5-Br	72∼77/2.5∼3	h	79.8	20.2	
	2-Cl	5-NO_2	105∼107/2	m	80.4	19.6	
	2-Cl	3,5-$(NO_2)_2$	m. p. 64	m	82.1	17.9	
	2-NCS	5-Br	135∼140/3	7	81.7	18.3	
	2-OH	5-NO_2	115∼118/2	h	92.1	7.9	
	2-OAc	5-Br	92∼96/2.5∼3	h	81.5	18.5	
	2-OAc	5-NO_2	m. p. 38∼39	h	8.5	3.4	88.1 (CCl_4)

* The sample contains 2-methyl-5-bromothiophene.

** The sample contains 3-methyl-2-bromothiophene.

a W. J. King and F. F. Nord, *J. Org. Chem.*, **14**, 638 (1949).

b F. F. Blicke and F. Leonald, *J. Am. Chem. Soc.*, **68**, 1934 (1946).

c Y. Matsuki and T. Sone, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **63**, 834 (1960).

d W. Steinkopf and W. Hanske, *Ann.*, **541**, 257 (1939).

e F. F. Blicke and J. H. Burckhalter, *J. Am. Chem. Soc.*, **64**, 477 (1942).

f Y. Matsuki and T. Sone, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zassi)*, **62**, 1559 (1959).

g W. S. Emerson and T. M. Patrick, Jr., *J. Org. Chem.*, **14**, 790 (1949).

h Y. Matsuki and T. Sone, unpublished work.

i E. Campaigne and W. M. LeSuer, *J. Am. Chem. Soc.*, **70**, 1555 (1948).

j Commercial product.

k "Org. Syntheses", Coll. Vol., **1**, 107 (1948).

l Ibid., **1**, 436 (1948).

m T. Sone and Y. Matsuki, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **83**, 496 (1962).

n H. R. Snyder et al., *J. Am. Chem. Soc.*, **79**, 2556 (1957).

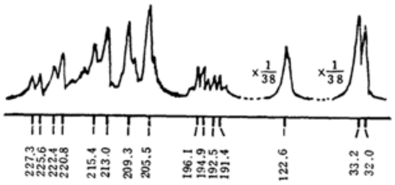
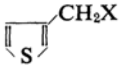
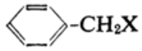


Fig. 1. The proton magnetic resonance spectrum of a mixture of 2-methyl-5-bromothiophene and 2-thenyl bromide at 40 Mc./sec. Applied magnetic field increases from left to right.

TABLE II. CHEMICAL SHIFTS OF THE METHYLENE PROTONS IN 2-THENYL, 3-THENYL AND BENZYL COMPOUNDS, REFERRED TO CYCLOHEXANE IN c.p.s. AT 40 Mc./sec.

Group X	Chemical shift, c. p. s.		
			
H	$33._5{}^{*1}$	27^{*1}	$28._5{}^{*2}$
CH_3	51		43
CN	$89._5$ (0.7^{*3})	$83._5$	$80._5$
COOH		86	83
NH_2	95 $(0.7_5{}^{*3})$		$87._5$
C_6H_5	97		$91._5$
SCN	107	101	95
C_4H_3S	111		97
OCH_3	120 (0.6^{*3})	$115._5$	113
Br	$122._5$	116	111
Cl	124		113
NCS	125		111
OH	$125._5$		$118._5$
OAc	148		141

^{*1} The measured condition is given in Ref. 2.
^{*2} The measurement was made for the solution containing 10 mol.% cyclohexane.
^{*3} Doublet spacing in c.p.s.

which we have obtained. Figure 1 shows the spectrum of a mixture of 2-methyl-5-bromothiophene and 2-thenyl bromide which was obtained by bromination of 2-methylthiophene with *N*-bromosuccinimide in the presence of benzoyl peroxide[6] and cannot be separated easily by distillation. At the highest field, $32._5$ c.p.s. referred to cyclohexane, there is the methyl proton peak of 2-methyl-5-bromothiophene which has the doublet structure with the coupling constant of 1.1_5 c.p.s. The next ill-resolved broad peak at $122._5$ c.p.s. corresponds to the methylene protons of 2-thenyl bromide. The peaks of the ring protons are rather complicated because of the overlapped signals of the two isomers. But it can be partially assigned as follows; two overlapped quartets at the highest field in the ring proton spectrum come from the 3-positioned proton in 2-methyl-5-bromothiophene and four peaks at the lowest field come from the 5-positioned proton in 2-thenyl bromide. The methylene proton peaks in these compounds are distinguished very clearly even with the measurements in the mixture. Chemical shifts of methylene protons in 2-thenyl, 3-thenyl and the corresponding benzyl derivatives are given in Table II. In the course of these studies, we have observed the thermal isomerization of 2-thenyl thiocyanate which easily occurs even at about 150°C[7,8]. But in the case of 3-thenyl thiocyanate, the thermal isomerization could not be observed under the same conditions so that it seems to be sure that 3-thenyl thiocyanate is more stable than 2-thenyl thiocyanate. The chemical shifts of methylene protons given for thenyl and benzyl isothiocyanate in Table II are those obtained from the thermal isomerization of the corresponding thiocyanates. It is seen from Table II that the methylene proton resonance peaks of 2-thenyl derivatives are observed usually at lower field than those of the corresponding 3-thenyl ones. The mean difference between them is about 6 c.p.s. A similar magnitude of the chemical shifts is also observed in thiophene where 3-protons are more shielded than 2-ones by about 6 c.p.s.[9,10,11] From Table II, the methylene protons of benzyl derivatives are more shielded than those of the corresponding 2-thenyl and 3-thenyl derivatives by about 9 and 3 c.p.s. as the mean value, respectively. It is very interesting to note that the ring protons of thiophene are more shielded than those of benzene, while, the methylene protons of thenyl derivatives are less shielded than those of the corresponding benzyl derivatives. This may arise from the difference between the circulating currents of π-electrons in benzene and the thiophene ring. Ring proton spectra of thenyl derivatives studied are rather complex for analyses. But the weighted mean chemical shift for three ring protons in each compound can be estimated from the observed spectrum, the results of which are given in Table III. The ring proton spectrum of each thenyl derivative spreads more widely as compared with the corresponding benzyl derivative. It means that the five ring protons in each benzyl derivative are rather magnetically equivalent, but it is not the case with the three

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[6] K. Dittmer et al., *J. Am. Chem. Soc.*, **71**, 1201 (1949).

[7] Y. Matsuki and T. Sone, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 2171 (1960).

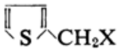
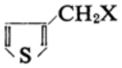
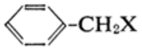
[8] K. Takahashi, T. Sone, Y. Matsuki and G. Hazato, This Bulletin, **33**, 1465 (1960).

[9] S. Gronowitz and R. A. Hoffman, *Arkiv för Kemi*, **15**, 45 (1959).

[10] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 2095 (1959).

[11] T. Isobe, *Bull. Chem. Res. Inst. Non-Aqueous Solutions, Tohoku Univ.*, **9**, 115 (1960).

Table III. Mean chemical shifts of the ring protons in 2-thenyl, 3-thenyl and benzyl compounds, referred to cyclohexane in c.p.s. at 40 Mc./sec.

Group X	Mean chemical shift, c.p.s.		
			
H	210^{*1}	211^{*1}	222
CH_3	210		224
CN	217	225	$227._5$
COOH		$224._5$	$228._5$
NH_2	$215._5$		$227._5$
C_6H_5	^{*2}		222
SCN	218	$226._5$	$228._5$
C_4H_3S	$213._5$		^{*2}
OCH_3	217	223	229
Br	218	$223._5$	226
Cl	$215._5$		$225._5$
NCS	^{*3}		^{*3}
OH	216		$226._5$
OAc	222		$229._5$

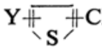
^{*1} The value was taken from Ref. 2.

^{*2} Not to be estimated because of overlapping.

^{*3} Not to be estimated because of the presence of the corresponding thiocyanate.

ring protons in each thenyl derivative. Of the two series of thenyl derivatives, as shown in Table III, the mean chemical shift of the ring protons is mainly affected by the position of the substituent in the ring to which the CH_2X group attached, and in this case, the substituent effect of X in the CH_2X group is unimportant. The Shoolery's method[12] for calculating the alkyl proton frequencies in acyclic systems is highly successful for systems of the type $Y-CH_2-X$[13]. His additivity rule is also applicable to the methylene protons of some benzyl derivatives[13] and the same will be the case with thenyl derivatives. In Table II, acetoxy group, which causes the methylene protons to shift to the lowest field side, is a very distinct one, such a case being not found in Shoolery's or Jackman's table[12,13]. Some of the substituted thenyl derivatives are also investigated and the results are summarized in Table IV. In the case where the signal is split by the indirect spin-spin interaction, the chemical shift given in Table IV is that for the center of the resonance pattern. The observed coupling constants between two ring protons, J_{34}, fall into the range of 3.7∼4.2 c.p.s., which are consistent with our previous assumption, $J_{34}\simeq 4.0$

Table IV. Proton magnetic resonace data for the substituted thenyl derivatives,


$Y-C_4H_2S-CH_2X$, referred to cyclohexane in c.p.s., at 40 Mc./sec.

Substituents		Chemical shift, c.p.s.					Coupling constant, c.p.s.	
X	Y	CH_3	CH_2	3-H	4-H	5-H	J_{34} or J_{45}	$J_{CH_2\cdot 3-H}$
2-CN	5-I		94	$208._5$	$223._5$	—	$J_{34}=3.7$	1.0
2-SCN	$3-NO_2$		$138._5$	—	$247._5$	$247._5$		
2-SCN	$5-CH_2SCN$		$114._5$	220	220	—		
2-SCN	$5-NO_2$		126	$232._5$	258	—	$J_{34}=4.1$	
3-SCN	$2-NO_2$		$129._5$	—	$233._5$	257	$J_{45}=5.5$	
$2-OCH_3$	5-Br	$71._5$	117	204	213	—	$J_{31}=3.7$	0.9
2-Br	$3-NO_2$		$141._5$	—	$243._5$	231	$J_{45}=5.5$	
2-Br	5-Br		$122._5$	210	210	—		
3-Br	$2-NO_2$		$134._5$	—	227	239	$J_{45}=5.1$	
2-Cl	5-Cl		$122._5$	208	$203._5$	—	$J_{34}=3.7$	0.7
2-Cl	5-Br		$123._5$	$205._5$	$211._5$	—	$J_{34}=3.7$	0.7
2-Cl	$5-NO_2$		$136._5$	226	252	—	$J_{34}=4.1_5$	0.8_5
2-Cl	$3,5-(NO_2)_2$		$159._5$	—	280	—		
2-NCS	5-Br		$128._5$	$208._5$	215	—	$J_{34}=3.8$	0.8
2-OH	$5-NO_2$		144	$225._5$	256	—	$J_{34}=4.1$	
2-OH	$3-NO_2$*		*	—	245	237	$J_{45}=5.4$	
2-OAc	5-Br	22	145	211	216	—	$J_{34}=3.9$	0.7
2-OAc	$5-NO_2$	$26._5$	$148._5$	221	$249._5$	—	$J_{34}=3.9$	

* The measurement was made for a mixture of 5-nitro- and 3-nitro-2-thenyl alcohols. The methylene peak was not observed because of overlapping.

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[12] J. N. Shoolery, *Tehchnical Information Bulletin, Varian Associates, Palo Alto, California*, **2**, No. 3 (1959).

[13] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, London (1959), pp. 59, 130.

c.p.s.[2], and also with the others[14]. The coupling constants observed between methylene protons and the 3-positioned ring proton in 2-thenyl derivatives fall into the range of 0.6 ~1.0 c.p.s. This kind of interaction between the ring proton and the methylene protons in thenyl derivative gives us some useful information for the assignments of the spectra, especially in the cases of small internal chemical shifts. For example, in 5-chloro-2-thenyl chloride, the assignment of the two ring protons was made by the observed multiplet structure, but the chemical shift between them is small, then the assignment was also ascertained by taking the spectrum at 56.4 Mc.[15] In all 5-substituted 2-thenyl derivatives tabulated in Table IV, except 5-chloro-2-thenyl chloride, the 3-positioned proton is more shielded than the 4-positioned one, respectively.

TABLE V. DISPLACEMENTS OF THE METHYLENE PROTON PEAKS WHEN THE SAMPLES ARE DILUTED WITH CYCLOHEXANE, CARBON TETRACHLORIDE AND ACETONE, IN c.p.s. AT 40 Mc./sec., REFERRED TO THE VALUES DILUTED WITH CYCLOHEXANE, MINUS SIGN SHOWING THE DISPLACEMENT TOWARD HIGHER FIELD

Compound	Solvent		
	Pure*	CCl_4	Acetone
Benzyl cyanide	−1.0	5.0	16.0
2-Thienylacetonitrile	0.5	5.0	18.0
3-Thienylacetonitrile	1.0	5.0	16.0
Benzyl thiocyanate	−3.5	4.5	15.5
2-Thenyl thiocyanate	−3.5	4.0	15.5
3-Thenyl thiocyanate	−2.5	3.0	13.5
5-Chloro-2-thenyl chloride	1.0	4.5	15.0
Benzyl methyl ether	−1.0	1.5	3.5
2-Thenyl methyl ether	−0.5	1.5	3.5
3-Thenyl methyl ether	0.0	0.5	3.5
Benzyl acetate	1.5	1.0	4.5
2-Thenyl acetate	2.5	1.0	5.0

* The values are estimated from Table II.

The observation of the solvent effects on the chemical shifts for methylene protons of several compounds was also made. Three typical solvents were used. The experiment was carried out with definite dilute solutions of the compounds in each solvent; those are 13.5 wt.% solutions in cyclohexane, 7.5 wt.% solutions in carbon tetrachloride containing 1.5 wt.% cyclohexane and 14 wt.% solutions in acetone containing 14 wt.% cyclohexane. The results are summarized in Table V. The values in pure liquid state in Table V are estimated from the values in Table II. It is seen from Table V that the displacements in question are much affected by the difference of X of the CH_2X groups and not so much by the difference between the corresponding benzyl, 2-thenyl and 3-thenyl derivatives.

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[14] S. Gronowitz and R. A. Hoffman, *Arkiv för Kemi*, **13**, 279 (1958); ibid., **16**, 563 (1960).

[15] The authors wish to express their thanks to Dr. N. Hayakawa (Japan Atomic Energy Research Institute) for providing the NMR spectrum of 5-chloro-2-thenyl chloride at 56.4 Mc.