^{13}C NMR Study of Chloro- and Methylthiophenium Ions

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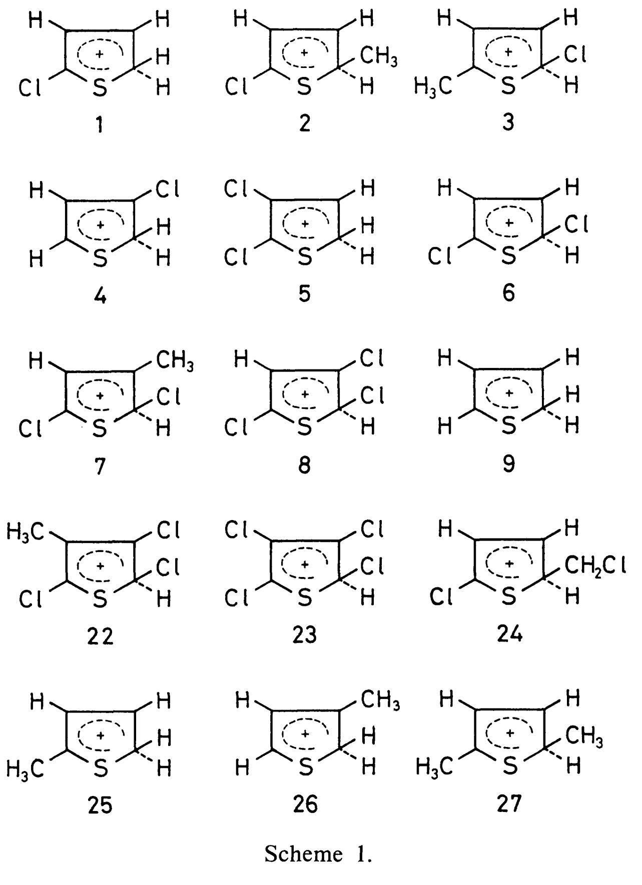
The ^{13}C NMR spectra of fifteen cations formed from chloro- and methylthiophenes were observed in HSO_3F solutions at −50 °C. Protonation occurred at one of the α-carbons in all of the cases studied. In these systems, the ^{13}C chemical shifts are classified into four ranges without overlapping. The result is useful for the identification of the carbons in the cationic species. Protonated protons in the cationic species can exchange intramolecularly and intermolecularly, even with those in solvents.

It has been reported that 2,5-dichlorothiophene reacts with active arenes in the presence of aluminum chloride to give 3-arylthiophene.[1] In this reaction, the formation of a protonated cationic intermediate seems to play an important role. Studies of various arenium ions in superacids have been energetically performed by many researchers.[2] Thiophene derivatives produce thiophenium ions in a superacid solution.[3] ^{1}H NMR spectra of chlorothiophenium ions were reported previously.[4] However, the ^{13}C NMR technique is superier to ^{1}H NMR because direct information can be obtained concerning positively charged carbons, and a wide observed range of signals is possible.[5] ^{13}C NMR data regarding thiophenium ions have not yet been reported, except for one species.[3b] We have directly observed the ^{13}C NMR spectra of the fifteen thiophenium ions given in Scheme 1. The numbering of the ions follows that used in a previous report.[4]



Scheme 1.

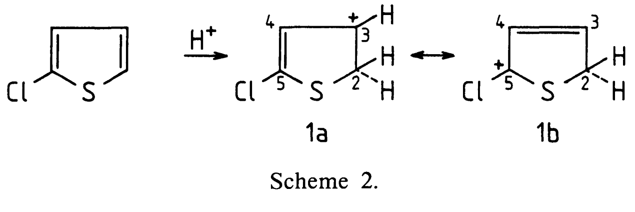
Experimental

The most starting materials used in this study were commercially available. Other starting materials were prepared by one of the present authors (T. S.). Commercial reagents were used in the experiments without any further purification. The HSO_3F–SbF_5 solution used was prepared by mixing HSO_3F and SbF_5 with a molar ratio of 1:0.44 under a nitrogen stream in a dry box. The acidity function of this solution (H_0) was assumed to be smaller than −20, and that of HSO_3F about −15.[6] The cationic sample was prepared at −78 °C by previously described procedures.[4] It was then kept in a dry ice–methanol bath at ca. −80 °C. The sample was moved in an NMR probe, which was precooled to about −50 °C.

^{13}C and ^{1}H NMR measurements were carried out by means of a Varian XL-200 spectrometer at 50.31 and 200 MHz, or a Hitachi R-20B spectrometer at 60 MHz, respectively. The chemical shifts were referred to the signal of tetramethylsilane (TMS) in a sealed Pyrex capillary inserted into each sample tube. Field/frequency locking was carried out using a stronger ^{2}D signal in CD_3OD, which was filled between two coaxial tubes (10 and 5 mm in diameter). Magnetic susceptibility corrections were necessary for comparing the two values measured with the superconducting and permanent magnet systems.[7]

Results and Discussion

The ^{13}C NMR chemical shifts of fifteen cations are given in Table 1. The sites of protonation and the reference numbers of the cations were the same as in the previous report, as shown in Schemes 1 and 2. Three



Scheme 2.

Table 1. ^{13}C Chemical Shifts of Protonated Chlorothiophenes in HSO_3F at −50 °C

No.	Substituent	Chemical shift/ppm				
		2C	3C	4C	5C	Me
1	5-Cl	60.44	180.40	143.77	219.45	
2	5-Cl, 2-Me	72.96	185.57	141.60	219.63	12.25
3	2-Cl, 5-Me	72.99	174.76	140.16	242.85	25.38
4	3-Cl	59.96	185.56	136.98	211.58	
5	4,5-Cl_2	55.73	172.99	143.27	216.23	
6	2,5-Cl_2	74.21	177.94	141.34	226.74	
7	2,5-Cl_2, 3-Me	73.49	200.95	139.41	221.02	19.53
8	2,3,5-Cl_3	72.08	185.31	139.45	222.05	
9	—	61.53	180.88	141.56	213.47	
22	2,3,5-Cl_3, 4-Me	69.02	179.65	148.59	221.65	11.75
23	2,3,4,5-Cl_4	67.99	177.25	140.08	218.45	
24	5-Cl, 2-CH_2Cl	77.73	181.09	143.77	219.49	38.45(CH_2)
25	5-Me	59.09	176.62	142.85	235.50	23.14
26	3-Me	60.74	204.08	139.80	210.05	20.24
27	2,5-Me_2	71.08	182.04	140.48	236.13	11.80(2Me), 23.59(5Me)

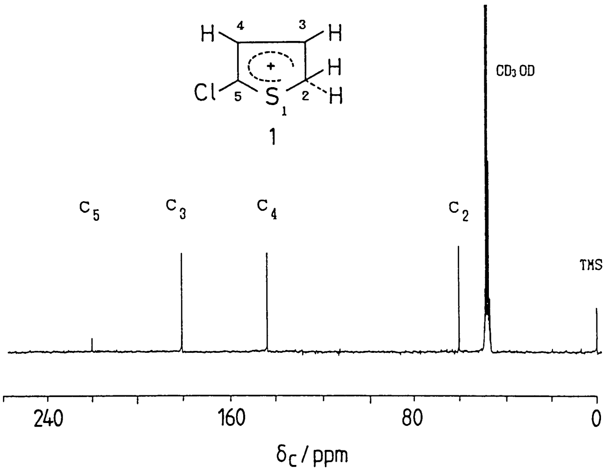


Fig. 1. ^{13}C NMR spectrum of **1** in HSO_3F at 50.3 MHz and −50 °C. There is no signal except for those of the four carbons of **1** and external locking and reference signals.

cations from **22** to **24** were prepared and then first described in the present article.[8] A typical ^{13}C NMR spectrum of **1** is given in Fig. 1. Four carbon signals of each species can easily be assigned from the standpoint of their chemical shifts. The observed chemical shifts were distinctly separated into four ranges without any overlapping. These ^{13}C chemical shifts are correlated with the ^{1}H chemical shifts and π-electron densities calculated by an ab initio STO-3G method.[9] They, however, are not correlated well with the total electron densities calculated by the STO-3G method. The fact that C_5 is more deshielded than C_3 shows that canonical structure **1b** is more important than **1a** in thiophenium ions.

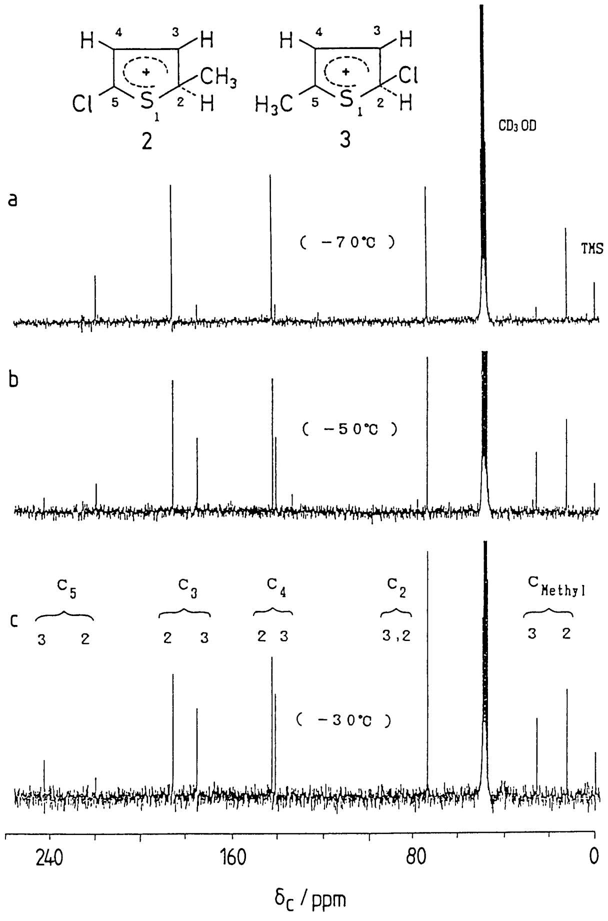


Fig. 2. ^{13}C NMR spectral changes of **2** and **3** in HSO_3F at 50.3 MHz. a) At −70 °C; b) at −50 °C; c) at −30 °C.

Methylchlorothiophenium Ions (2 and 3). The ^{13}C NMR spectra of **2** and **3** are given in Fig. 2. Paired ^{13}C signals changed their relative intensities with increasing temperature. The conversion from **2** to **3** was irreversible with the temperature. The results are consistent with those previously observed by ^{1}H NMR, which is characterized by a 2,5-hydrogen shift.[4] The populations of **2** and **3** are given in Table 2; they were evaluated by integrating the ^{1}H NMR signals. It is

Table 2. Ratio of Production and ^{13}C NOE data for **2** and **3**

Temperature	Ratio of production (**2**:**3**)			
°C	HSO_3F		HSO_3F+SbF_5	
−70	92: 8	(2.9)[a]	86:14	(2.9)
−60	91: 9	(2.9)	—[b]	
−50	66:34	(2.9)	84:16	(2.9)
−40	56:44	(2.0)	—[b]	
−30	55:45	(2.0)	82:18	(2.9)
−10	53:47	(1.0)	78:22	(2.6)
0	—[c]		71:29	(2.5)
+10	—[c]		56:44	(1.4)

a) Data of parentheses are ^{13}C NOE data for C_2 carbons. b) Measurements were not done. c) The cations decomposed.

supposed that the conversion rate is perturbed by changing the acidity function (H_0) of the superacid. A decrease in the acidity function decreases the selectivity of the protonation site. For example, the ratio of **2** over **3** in HSO_3F (11.5) is larger than that in HSO_3F–SbF_5 (6.1) at −70 °C. The stability of cations **2** and **3**, however, increases in a strong superacid. The ratio of **2** over **3** is almost constant at temperatures from −70 to −60 °C in HSO_3F, and from −70 to −30 °C in HSO_3F–SbF_5. Moreover, the cations decomposed at 0 °C in the former solution. Therefore, **2** and **3** are more stable in the latter solution than in the former solution.

NOE measurements were carried out to clarify that the conversion from **2** to **3** occurs either intramolecularly or intermolecularly (for example, via proton exchange with the solvent). Since the NOE value provides information concerning the connectivity of the C–H bond, NOE of C_2 in **2** or **3** was measured. The results are given in Table 2. NOE decreased from about 2.9 to 1.0 with a temperature rise from −50 to −10 °C. From Table 2, in the case of HSO_3F, the conversion from **2** to **3** begins with an intramolecular proton exchange at −50 °C. Above −20 °C, an intermolecular exchange of a proton will occur, even with that in the solvent. In the case of a HSO_3F–SbF_5 system, however, full NOE of the sample has been observed from −70 to −30 °C. It still has a decreased NOE of 1.4 even at 10 °C. After this measurement, when the sample was again cooled down to −50 °C, the NOE of the C_2 signal recovered to about 2.6. These results show that in a HSO_3F–SbF_5 system no intermolecular exchange of protons occurs between the cations and the solvent.

In temperature-variable experiments the ^{13}C chemical shifts slightly changed with the temperature. A typical example is shown in Fig. 3. For ions **2** and **3**, all of the signals move slightly downfield with increasing temperature. The chemical shift changes of C_4 are almost parallel for **2** and **3**. However, the behaviors of C_3 and C_5 are different. This seems to be affected by the position and kind of substituent. A chlorine atom seems to have a larger effect than does a methyl group.

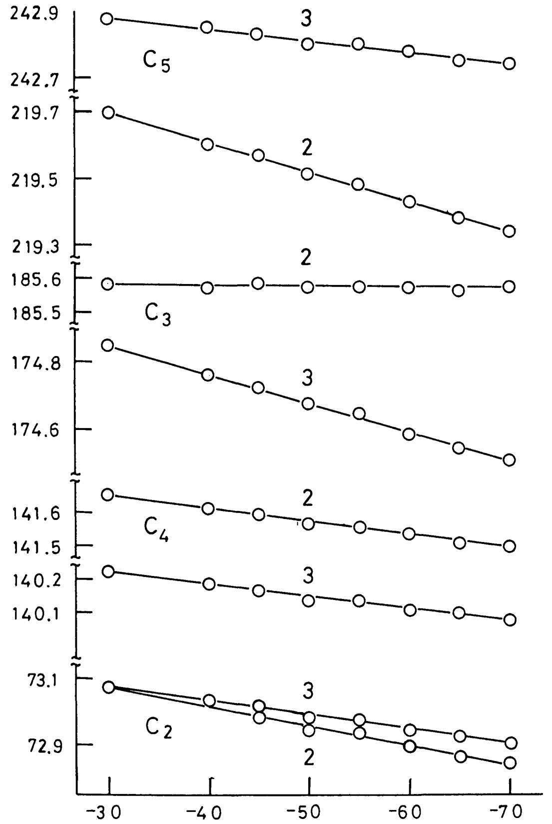


Fig. 3. ^{13}C chemical shifts (ordinate in ppm) of **2** and **3** in HSO_3F as a function of the temperature (abscissa in °C) at 50.3 MHz.

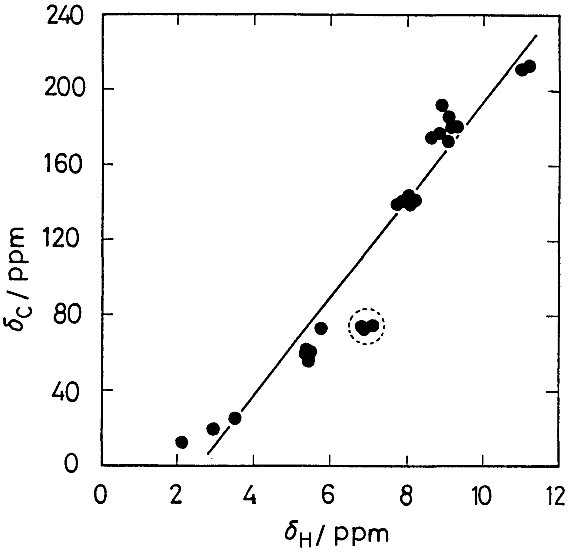


Fig. 4. Correlation of ^{13}C (ordinate) and ^{1}H (abscissa) chemical shifts for the adjacent carbon and hydrogen atoms in the chlorothiophenium ions.

The chemical-shift changes between **2** and **3** are larger for C_3 and C_5 than for C_4. The behavior of the C_3–C_4–C_5 skeleton seems to be similar with that of the allylic ion.[2b)] In the system, the sensitivity of C_3 or C_5 is larger than that of C_4 for any change. This can be explained by the selfpolarizabilities of C_3, C_4, and C_5, which were evaluated to be 0.442, 0.354, and 0.442, respectively, using simple HMO theory without considering the neighbors.

^{13}C and ^{1}H Chemical Shifts of Chlorothiophenium Ions. In ionic species, such as carbocations, an extra charge has a greater effect on both the ^{13}C and ^{1}H chemical shifts than do any other factors. A correlation between the ^{13}C and ^{1}H chemical shifts is given in Fig. 4. Twenty eight sample points are correlated with a correlation coefficient of r=0.955. Several C_2 data of 2-substituted ions among 28 data, however, are specific, since they are plotted below the correlated straight line, as indicated by the circle in Fig. 4. This shift in the deshielded direction is considered to be due to the exchange of H_2 with solvent protons. The line widths of C_2 seem to be broader than those of the other carbons. The broadening may be ascribed to an exchange effect between H_2 and the solvent protons. This exchange seems to be promoted by 2-positioned chlorine. In the case of 2-methylsubstituted cations, however, the C_2 shifts are plotted on the correlated straight line. The straight line for 24 data gives a correlation coefficient of r=0.983, except for four C_2 shifts of 3, 6, 7, and 8. The correlated line has a slope of 26.0, which is larger than 17.2 for the benzene system considered by Stothers.[5b)] This apparent linear dependency of the ^{13}C and ^{1}H shifts means that both the ^{13}C and ^{1}H chemical shifts are controlled mainly by excess positive charge within series of closely related species.

^{13}C Substituent Chemical Shifts. The ^{13}C SCS are given in Table 3; they were evaluated for eight observed cations at −50 °C. The substituents are the chlorine atom and the methyl group in the present article. The SCS values of thiophenes must be expressed as $S(\mathrm{X})_{\mathrm{ab}}$, where a and b indicate the positions of the given substituent X and the carbon in question.[10)] This notation must also be applied to the present case of thiophenium ions. The ^{13}C nuclei in question are classified as being two kinds of carbons, sp^3- or sp^2-hybridized one. The latter are affected by both inductive and mesomeric effects of the substituents. The former carbons, however, are mainly affected by the inductive effect. As can be seen in Table 3, $S(\mathrm{Cl})_{22}$ is the largest one among all S(Cl) values. This value is defined as that of the sp^3-hybridized carbons. On the other hand, $S(\mathrm{Me})_{33}$ is the largest one among all S(Me). S_{33} and S_{55} are similar in magnitude for both the chlorine and methyl groups. They are affected by two effects, inductive and mesomeric. S_{44} is smaller than for S_{33} or S_{55} for both chlorine and methyl groups. This is ascribed to a characteristic nature of the center carbon in an allylic moiety of a C_3–C_4–C_5 skeleton.

^{13}C Chemical Shifts and Electron Densities. ^{13}C chemical shifts are plotted in Fig. 5 against the total electron densities of each carbon atom (q_T) calculated by the STO-3G method.[9)] The points in Fig. 5 are roughly dispersed and seem to be weakly correlated with q_T. This seems to be due to the complex nature of the chemical shifts. Therefore, another correlation is shown in Fig. 6, where the shift differences between the cations and the starting materials are taken into consideration. This latter method seems to cancell other factors, except for the charges. The plotted points are limited for those in **1**, **4**, and **9**, where no steric interactions exist between substituents. The correlation coefficient is 0.960, except for those data of C_2. The slope of the correlated straight line is 169 ppm/electron,

Table 3. ^{13}C SCS Values of 2-Protonated Chloro- and Methylthiophenes[a)]

Parameter	SCS/ppm			
	i= 2	3	4	5
$S(\mathrm{Cl})_{2i}$	13.8	−2.5	−2.4	7.3
	(5.0)	(−0.8)	(−0.3)	(−1.0)
$S(\mathrm{Cl})_{3i}$	−1.6	4.7	−1.6	−1.9
	(−5.3)	(−1.3)	(0.7)	(0.9)
$S(\mathrm{Cl})_{4i}$	−4.7	−7.4	−0.5	−3.2
	(0.9)	(0.7)	(−1.3)	(−5.3)
$S(\mathrm{Cl})_{5i}$	−1.1	−0.5	2.2	6.0
	(−1.0)	(−0.3)	(−0.8)	(5.0)
$S(\mathrm{Me})_{2i}$	12.0	5.4	−2.4	0.6
	(14.5)	(−1.7)	(0.0)	(−2.1)
$S(\mathrm{Me})_{3i}$	−0.8	23.2	−1.8	−3.4
	(−4.6)	(10.7)	(2.4)	(0.0)
$S(\mathrm{Me})_{4i}$	−3.1	−5.7	9.1	−0.4
	(0.0)	(2.4)	(10.7)	(−4.6)
$S(\mathrm{Me})_{5i}$	−2.4	−4.3	1.3	22.0
	(−2.1)	(0.0)	(−1.7)	(14.5)

a) Data of parentheses are SCS for the neutral molecules in $CDCl_3$. Data of 2-chloro- and 2-methylthiophene are cited from Ref. 13.

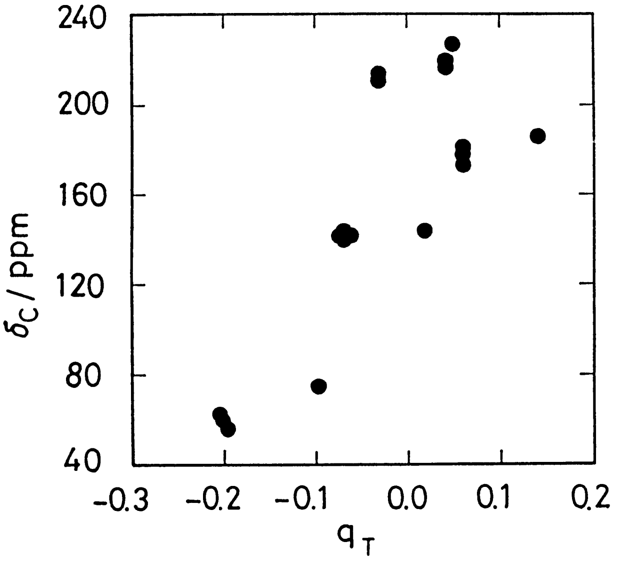


Fig. 5. Plots of the ^{13}C chemical shifts (ordinate) against the total charge densities (abscissa) of carbons for chlorothiophenium ions calculated by the STO-3G method.

Table 4. ^{13}C Chemical Shifts, $^1J_{CH}$, and ^{13}C NT_1 data for 2-Protonated Methylthiophenes in HSO_3F at 30 °C

No.	Substituent	Chemical shift/ppm				
		2C	3C	4C	5C	Me
		59.37	176.84	143.29	236.12	23.35$^{a)}$
25	5-Me	145	181	182	—	133$^{b)}$
		9.2	8.0	9.5	37.2$^{d)}$	27.6$^{c)}$
		61.07	204.62	140.20	210.03	20.47
26	3-Me	144	—	182	187	132
		7.4	23.7$^{d)}$	7.0	5.2	20.7
		71.63	182.47	140.88	236.64	12.08, 23.80
27	2,5-Me_2	143	179	181	—	136 133
		6.1	3.8	7.0	13.2$^{d)}$	12.6 14.4
						(2Me) (5Me)

a) ^{13}C chemical shifts for 2-protonated methylthiophenes. b) One-bond carbon-proton coupling constants in Hz. c) ^{13}C T_1 values multiplied with number (N) of adjacent protons in s. d) Net ^{13}C T_1 values for quaternary carbons.

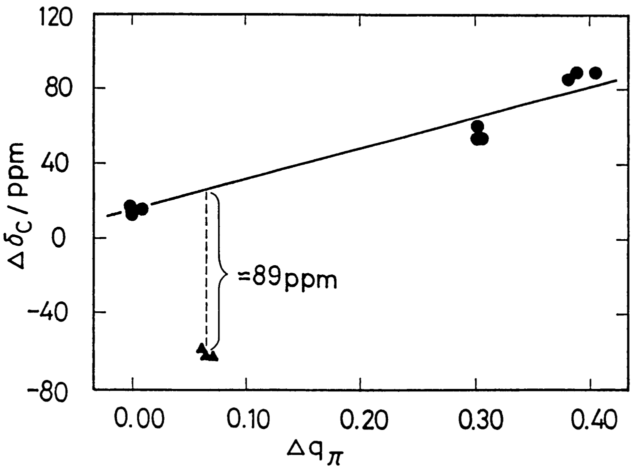


Fig. 6. Correlation of the ^{13}C chemical shift differences in **1**, **4**, and **9** against the π-charge-density differences of the carbons, calculated by the STO-3G method.

which is roughly consistent with that previously reported.[11] The C_2 values are out of range, as shown in Fig. 6. The deviation is ascribed to a hybridization change between cations and the starting materials from sp^2 to sp^3. It is estimated to be about 89 ppm. This value is consistent with that evaluated to be 92 or 97 ppm for the arylmethanide ions.[12]

One-Bond Carbon Proton Coupling Constants and ^{13}C Relaxation Times. It is considered that one-bond C-H coupling constant is a good index of the s-character of the carbon atom.[5c] Several values for stable thiophenium ions are given in Table 4. They are compared with those of the neutral precursors.[13b] The increase of $^1J_{CH}$ for C_3 and C_4 is about 15—20 Hz, which is ascribed to an effect of the localized positive charge. Those for C_2 are nearly 145 Hz and show its sp^3-hybridized character. The greater values compared with those of neutral hydrocarbons (about 125 Hz for sp^3-hybridized carbon[5c]) are ascribed to the positively charged character of the adjacent carbon.[14]

^{13}C T_1 studies can provide useful information concerning the rapid molecular motions in the specific system studied. To obtain such T_1 data, stable cations were measured at 30 °C in HSO_3F. The results are given in Table 4. Since ^{13}C T_1 are governed mainly by the dipole-dipole interaction, the smallest T_1 of carbon atoms in the molecule is interesting; they were found at C_3, C_5, or C_3 for **25**, **26**, or **27** respectively. Therefore, the axis through C_3 and the center of C_5 and sulfur is nearly one of the principal rotational axis of these cationic species. The molecular rotational motion is more rapid in the order of **25**, **26**, and **27** based on a comparison of the suitable nucleus in each species. For example, NT_1 of the 5-CH_3 carbon of **25** is about twice that of **27**. Therefore, the rotational motion of **25** is more rapid than **27**. This is quite reasonable from a molecular weight consideration of the cation. Further, the T_1 values of the ring carbons of these cationic species can be compared with those of the neutral ones. The values of **25**, for example, are about half of the corresponding values of the neutral molecules.[15] The molecular motion of the former cationic species is slower than that of the latter neutral molecule because the former strongly interacts with solvent molecules.

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7) Magnetic susceptibility corrections were found to be 0.535 ppm for the values in HSO_3F solution at 200 MHz and −0.267 ppm for those at 60 MHz respectively. When the values at 200 MHz were added by 0.802 ppm they can be compared with those measured at 60 MHz in Ref. 4.

8) The ^{1}H chemical shifts are 6.71, 2.61 for **22**, and 6.92 for **23**, and 6.05, 9.04, 7.98, and 4.62 ppm for H_2, H_3, H_4, and CH_2 of **24**, respectively. The values were measured at 200 MHz and were converted to those at 60 MHz for the comparison's purpose with the previously reported values by adding 0.802 ppm.

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