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NMR Study of Protonated Halothiophenes. II. An *ab Initio* Self-consistent Field Calculation of the Protonation of Chlorothiophenes

Yukihide Yamashita, Hiroyuki Kobayashi, Akihiro Yoshino,
Kensuke Takahashi,* and Tyo Sone†
Department of Industrial Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466
†*Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Jonan, Yonezawa 992*
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The STO-3G method was applied to the protonation of thiophene and chlorothiophenes. The optimized structures and charge densities thus obtained are consistent with the experimental results obtained from the ^{1}H NMR spectral data. In the neutral molecule, the β-chloro substituent lowers the total energy more than the α-one; however, the latter stabilizes the protonated state more than the former.

We have observed the halothiophenium ions produced from halothiophenes at rather low temperatures.[1-4] The NMR parameters thus obtained are useful in discussing the properties of such ions. Molecular orbital calculations are also done as supplements to the experimental results. Such calculations have previously been done by many researchers.[4-6] The system of thiophenes has the problem of whether the calculations should be carried out with or without the d-orbitals on the sulfur atom.[7]

This study has been performed by using the minimal basis set, the so-called STO-3G method.[8] The method is a very simple *ab initio* calculation and has a problem as to the quantitative determination of the properties.[9] However, the results are good enough to discuss the problems qualitatively.

Procedure

The calculation was carried out by using the HITAC M-200H computer and the Library Program (IMSPAK) installed in the Computer Center, Institute of Molecular Science, at Okazaki. The basis wave functions used were the STO-3G minimal basis set.[10] For the optimization of the structure, an initial structure was taken from that obtained by Bak *et al.*,[11] while the distance of the C–Cl bond was taken from that of Harshbarger *et al.* (1.7095 Å).[12] The structure of the thiophenium ion was assumed to be on a plane except for the atoms bonded to the protonated sp^3-carbon, which has an initial bonding angle with two out-of-plane atoms of 109.5°.

For chlorothiophenium cations, the SCF initial molecular orbitals were composed from those of the anionic ones because, when they were composed from the cationic ones, the SCF calculations did not converge with the optimized structures.

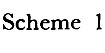
Results and Discussion

Structure of Thiophene, Chlorothiophenes, and Their Cations. The optimized structures of thiophene are given in Table 1, along with its experimental results and other calculated values. The values obtained by the STO-3G method are shorter in the double bond and longer in the single bond than those calculated by Amato *et al.*[13]

Table 1. Comparison of structure determinations of thiophene

Bond length	Bak *et al.* (1961) l/Å	Amato *et al.* (1982) l/Å	This work l/Å
S-C	1.7140±0.0014	1.726	1.732
C=C	1.3696±0.0017	1.348	1.335
C-C	1.4232±0.0023	1.432	1.454
C_α-H	1.0776±0.0015	1.067	1.079
C_β-H	1.0805±0.0014	1.069	1.080
Bond angle	θ/°	θ/°	θ/°
∠CSC	92.17±0.1	91.2	90.4
∠SCC	111.47±0.3	111.8	112.7
∠SCH	119.85±0.8	120.7	120.4
$\angle C_3C_4H_4$	124.27±0.1	123.6	123.1
∠CCC	112.45±0.2	112.6	112.1

The optimized structures of chlorothiophenes and their cations are summarized in Figs. 1 and 2. The ring-interior-angle of the substituted carbons of chlorothiophenes increases, while the bond lengths concerned with the carbons generally increase, as compared with those calculated for thiophene. Further, the bond-lengths of the C_β-H and the C_β-Cl bonds are longer than those corresponding to the C_α-H and the C_α-Cl bonds. As would be expected, the bond angles of the protonated carbons approach the tetrahedral angle. Since only one 3*H*-thiophenium ion has been calculated, the discussion of the cations will hereafter be limited to the 2*H*-thiophenium ions. In the protonated state, the bond lengths of the C_2–C_3, the C_4–C_5, and the S–C_2 bonds increase, while the reverse shortening appears in the C_3–C_4 and the S–C_5 bonds. These features are expressed schematically in Scheme 1. The C–H bond length increases in the order of the 4-, 3-, and 5-positions in the thiophene ring of the cationic state as compared with that in the neutral molecule; however, conversely, the C–Cl bond lengths decrease in the same order. On the other



Scheme 1.

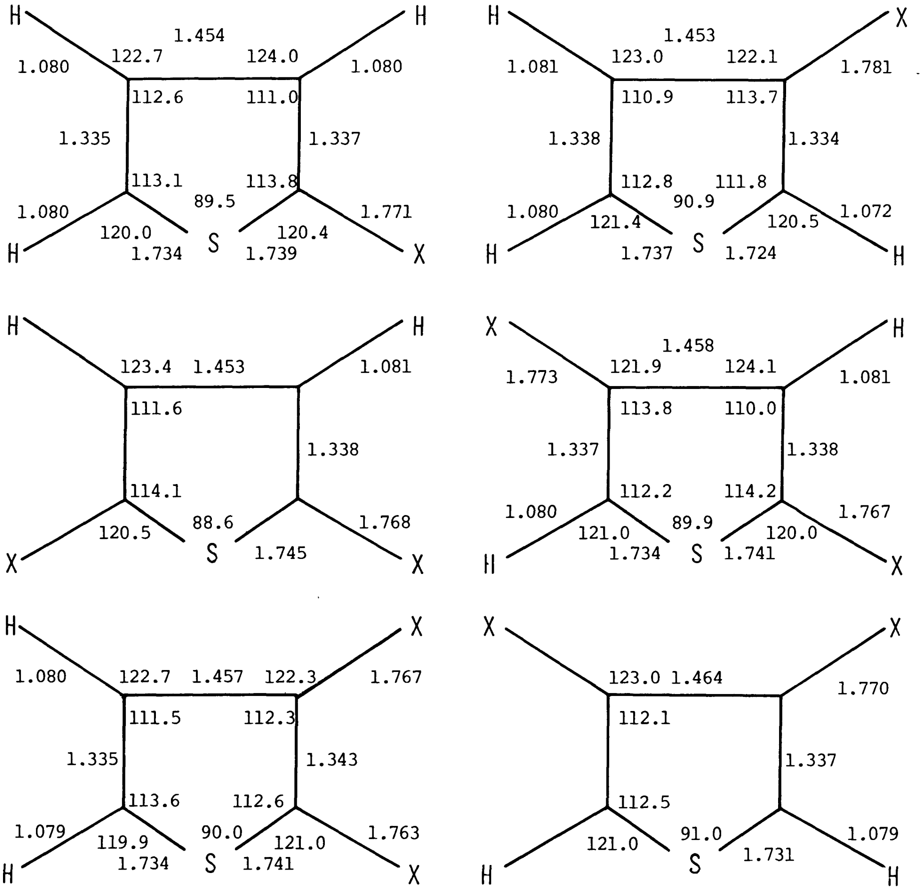


Fig. 1. Comparison of optimized geometries for chlorothiophenes. Bond lengths in Å and angles in degrees. X denotes chlorine atom.

Table 2. Total charges of thiophene, chlorothiophenes, and their cations as obtained by closed-shell-SCF calculations with a minimal basis set

	S	C_2	C_3	C_4	C_5	$X_{2(1)}$	$X_{2(2)}$	X_3	X_4	X_5
Thiophene	0.254	−0.177	−0.084	−0.084	−0.177	0.071		0.063	0.063	0.071
2-Cl	0.293	−0.074	−0.074	−0.076	−0.171	−0.136		0.084	0.074	0.081
3-Cl	0.285	−0.171	0.024	−0.075	−0.169	0.093		−0.152	0.083	0.083
2,5-Cl_2	0.328	−0.070	−0.067	−0.067	−0.070	−0.120		0.093	0.093	−0.120
2,3-Cl_2	0.317	−0.072	0.029	−0.069	−0.164	−0.103		−0.119	0.091	0.091
2,4-Cl_2	0.320	−0.068	−0.066	0.030	−0.165	−0.118		0.101	−0.135	0.101
3,4-Cl_2	0.311	−0.164	0.028	0.028	−0.164	0.101		−0.120	−0.120	0.101
2*H*	0.471	−0.205	0.060	−0.074	−0.031	0.153	0.153	0.155	0.143	0.174
2*H*,5-Cl	0.474	−0.202	0.061	−0.069	0.043	0.155	0.155	0.160	0.151	0.071
2*H*,3-Cl	0.477	−0.202	0.139	−0.070	−0.031	0.160	0.160	0.035	0.154	0.178
2*H*,3,5-Cl_2	0.480	−0.200	0.139	−0.066	0.043	0.162	0.162	0.041	0.162	0.078
2*H*,2,5-Cl_2	0.491	−0.097	0.059	−0.062	0.050	0.170	−0.027	0.169	0.158	0.089
2*H*,4,5-Cl_2	0.492	−0.197	0.060	0.018	0.043	0.160	0.160	0.170	0.001	0.094
2*H*,3,4-Cl_2	0.495	−0.199	0.138	0.016	−0.028	0.165	0.165	0.054	0.005	0.189

hand, the 3- and 5-(C–H) bonds are longer than those of the neutral molecules, although the situation is reversed with the 3- and 5-(C–Cl) bonds. This shows that the resonance effect of the chlorine atom plays a role in the cationic state. The expected structural model shown in Scheme 1 is consistent with the experimental finding that the values of J_{34} (*ca.* 5.5 Hz) are larger than those of J_{45} (*ca.* 4.0 Hz) in halogeno-substituted 2*H*-thiophenium ions.[2,3]

Charge Distributions. The total and π electronic charges of thiophene, chlorothiophenes, and their cations are tabulated in Tables 2 and 3. The protonations of these molecules occurred at the most negative carbons expected from the present calcula-

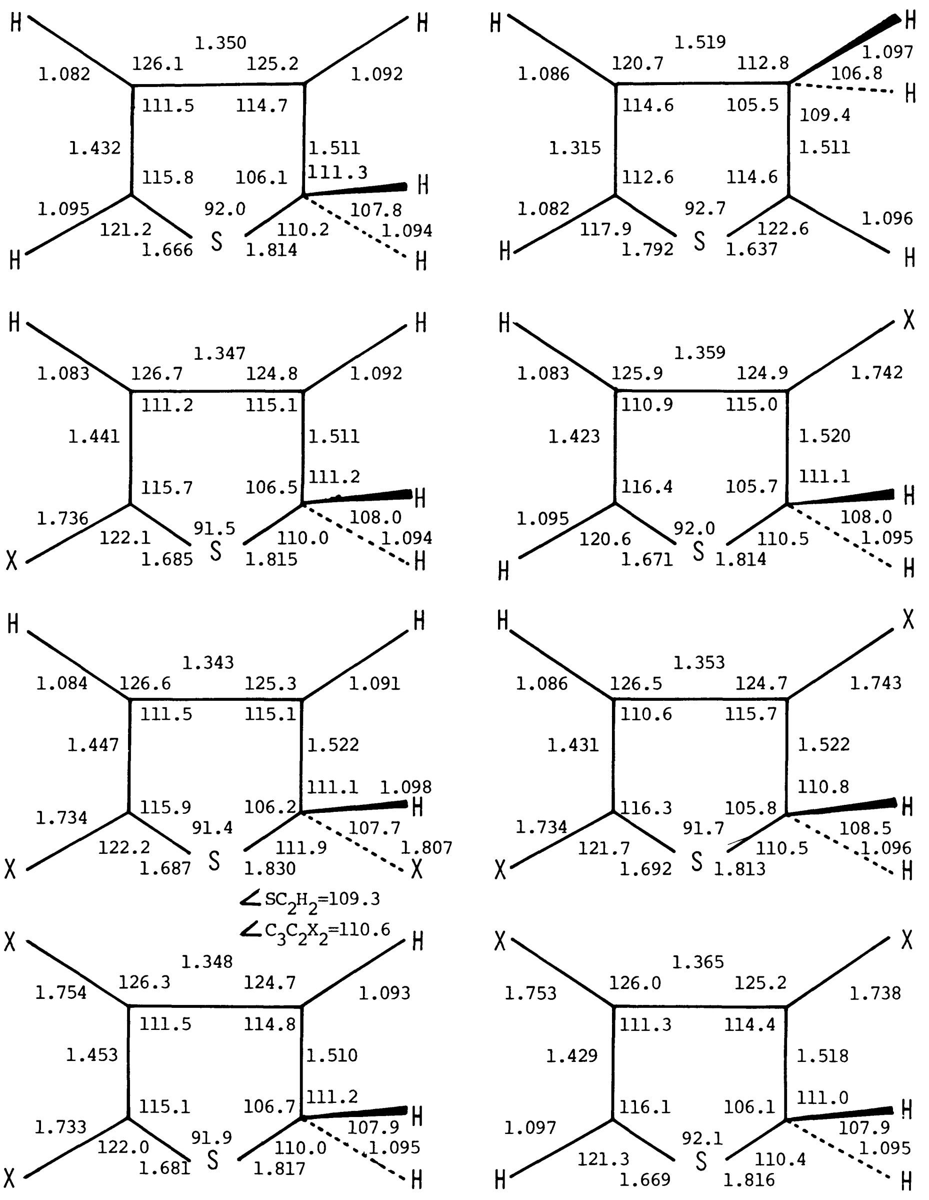


Fig. 2. Comparison of optimized geometries for thiophenium ions. Bond lengths in Å and angles in degrees. X denotes chlorine atom.

tions. However, the ^{1}H NMR chemical shifts are not directly proportional to the calculated charge densities on the hydrogen atoms for the neutral molecules.

In the cationic states, the chlorine atoms all have a positive charge except for the atoms bonded to the sp^3-hybridized carbon. This shows that the resonance effect of the chlorine atom is important in the cationic state. Table 3 shows that the positive charges on the thiophenium ions are localized more at the 5-carbon than at the 3-carbon. Table 4 summarizes the π-charge-density differences between the neutral molecules and the corresponding cations. From the table, the excess π-charge densities can be seen to be located more at the 5-carbon than at the 3-carbon. For the thiophenium ions, the calculated electronic densities of the hydrogens bonded to the sp^2-hybridized carbons are proportional to the observed ^{1}H chemical shifts, as is shown in Fig. 3. The proportional coefficient is about 100 ppm/electron. The dotted lines in the figure show that the chlorine substituents cause a shielding effect in spite of attracting the electron from the hydrogens. The coefficients of the dotted lines are −25, −35, and −58 ppm/electron, from the bottom to the top in the figure. These values show the effects of the charge on the 4-, the 3-, and the 5-hydrogens respectively.

Energies. The total calculated energies of thiophene, chlorothiophenes, and their protonated species are given in Table 5. The total energies of the molecules are dependent upon the methods used. The values for thiophene obtained with several methods are shown in the table. The β-chloro substituent lowers the energy more than does the α-one. The α-protonation lowers the energy more than does the β-one in thiophene; the difference is about 48 kJ mol^{-1} (0.01877 a.u.). This result is consistent with the experimental result reported in the previous study, in which only the α-protonation products have been observed, but not the β-ones.[2)]

The following schemes can be considered from the total-energy consideration of Table 5. In each case, the right system is more stable than the left system. Therefore, the protonation of thiophene is easier than that of

Table 3. π-Orbital charges of the ring atoms of thiophene, chlorothiophenes, and their cations obtained by closed-shell-SCF calculations with a minimal basis set

	S	C_2	C_3	C_4	C_5
Thiophene	0.230	−0.071	−0.046	−0.046	−0.071
2-Cl	0.226	−0.117	−0.034	−0.045	−0.066
3-Cl	0.234	−0.062	−0.095	−0.052	−0.058
2,5-Cl_2	0.221	−0.111	−0.034	−0.034	−0.111
2,3-Cl_2	0.230	−0.111	−0.085	−0.050	−0.054
2,4-Cl_2	0.230	−0.103	−0.042	−0.092	−0.059
3,4-Cl_2	0.240	−0.052	−0.100	−0.100	−0.052
2*H*	0.410	—	0.260	−0.059	0.334
2*H*,5-Cl	0.377	—	0.257	−0.064	0.272
2*H*,3-Cl	0.393	—	0.208	−0.063	0.324
2*H*,2,5-Cl_2	0.368	—	0.241	−0.054	0.292
2*H*,3,5-Cl_2	0.360	—	0.204	−0.068	0.263
2*H*,4,5-Cl_2	0.392	—	0.244	−0.104	0.266
2*H*,3,4-Cl_2	0.405	—	0.196	−0.105	0.320

Table 4. Additional π-orbital charges of the ring atoms of the thiophenium ion and chlorothiophenium ions

	S	C_2	C_3	C_4	C_5
2*H*	0.180	—	0.306	−0.013	0.405
2*H*,5-Cl	0.151	—	0.302	−0.030	0.389
2*H*,3-Cl	0.159	—	0.303	−0.011	0.382
2*H*,2,5-Cl_2	0.147	—	0.275	−0.020	0.403
2*H*,3,5-Cl_2	0.130	—	0.296	−0.026	0.366
2*H*,4,5-Cl_2	0.162	—	0.294	−0.019	0.377
2*H*,3,4-Cl_2	0.165	—	0.296	−0.005	0.372

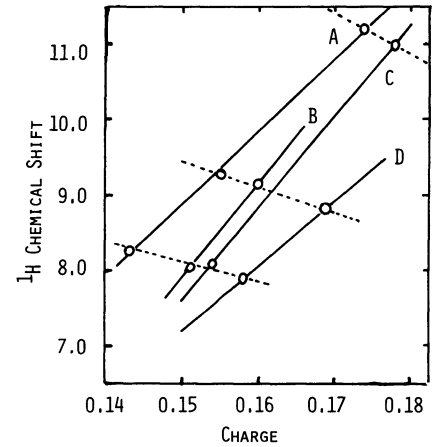
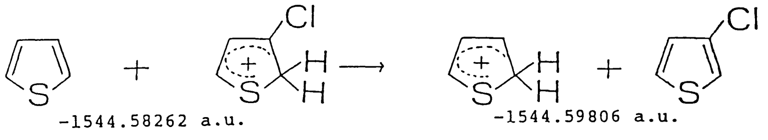


Fig. 3. Correlation of ^1H chemical shifts of protons attached to the sp^2-hybridized carbons with total calculated charges in thiophenium and chlorothiophenium ions; A, thiophenium ion; B, 2*H*-5-chloro-; C, 2*H*-3-chloro-; D, 2*H*-2,5-dichlorothiophenium ions.

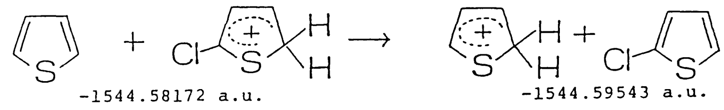
Table 5. Calculated total energies of thiophene, chlorothiophenes, and their cations

Thiophene	−545.09237 a. u.
	−550.4174[a)]
	−550.5353[a)]
	−550.66185[b)]
2-Cl	−999.09392
3-Cl	−999.09655
2,3-Cl_2	−1453.09271
2,4-Cl_2	−1453.09521
2,5-Cl_2	−1453.09289
3,4-Cl_2	−1453.09517
2*H*	−545.50151
3*H*	−545.48274
2*H*,5-Cl	−999.48935
2*H*,3-Cl	−999.49025
2*H*,2,5-Cl_2	−1453.46314
2*H*,3,5-Cl_2	−1453.47739
2*H*,4,5-Cl_2	−1453.47021
2*H*,3,4-Cl_2	−1453.47100

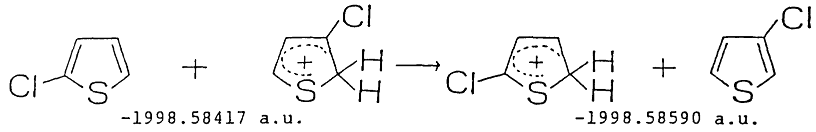
a) See Ref. 7b, b) See Ref. 13.



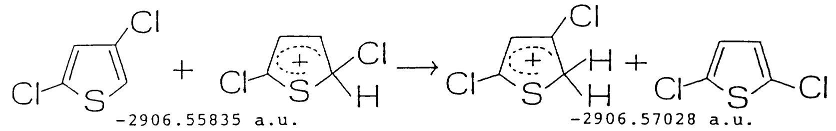
Scheme 2.



Scheme 3.

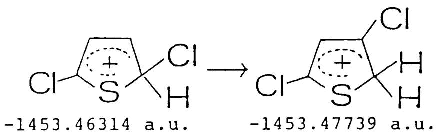


Scheme 4.



Scheme 5.

chlorothiophene. Scheme 4 is essentially interesting, for the chlorine substituent stabilizes the neutral molecule at the β-position more than at the α-position. However, Scheme 4 shows that the α-substituent is more effective than the β-one for the protonation. In other words, the resonance stabilization effect is stronger in the α-chlorine than in the β-one in the protonated state. Other interesting schemes appear below. The 2,4-dichlorothiophenium ion is more stable than the 2,5-one. However, the rearrangement has not occurred from the 2,5-dichlorothiophenium ion to the 2,4-one in the experiments,[1,2] though such a rearrangement has been observed in the dibromothiophenium ions.[3]



Scheme 6.

Conclusion

The STO-3G method was applied to the protonation of thiophene and chlorothiophenes. The optimized structures and charge densities thus obtained are consistent with those expected from the ^{1}H NMR spectral observations. The β-chlorine atom lowers the total energy more than the α-one in the neutral molecules; however, the latter substituent is more effective than the former in the resonance stabilization of the cationic state of the molecules.

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