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^{13}C NMR Spectra of Substituted 2-Thiophenecarboxylic Acid Methyl Esters and MNDO Calculations

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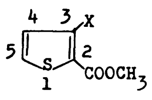
The ^{13}C NMR spectra have been reported on substituted 2-thiophenecarboxylic acid methyl esters. The chemical shift of ring carbons in methyl (4- and 5-substituted 2-thiophenecarboxylate)s was correlated linearly with that of the corresponding carbons in substituted thiophenes. Plots of the ^{13}C–H coupling constants of methyl (substituted 2-thiophenecarboxylate)s against those of substituted thiophenes showed a good linear relation. The ^{13}C NMR data were interpreted by the stable conformation and percent *s* character of C–H bonds obtained by MNDO calculation.

The ^{1}H NMR spectra of methyl (3-substituted 2-thiophenecarboxylate)s (**1**), methyl (4-substituted 2-thiophenecarboxylate)s (**2**), and methyl (5-substituted 2-thiophenecarboxylate)s (**3**), were reported by one of the present authors,[1] and the effects of the substituents were discussed.[1] The additivity rule for the ^{1}H chemical shifts of simple substituted thiophenes was applicable to the ring protons in the compounds of series **2** and **3**, but inapplicable to those in the compounds of series **1**. Based on the facts we examined the ^{13}C NMR spectra of substituted 2-thiophenecarboxylates of these three series. Similar deviation from the additivity rule has also been observed by ^{13}C chemical shift of some 2,3-disubstituted thiophenes by the present authors. The deviation will be due to steric and electronic interaction between the neighboring substituents on thiophene ring. The conformational change may affect on the deviation, because the anisotropy caused by substituents as well as the attractive interaction between substituents considerably perturbs ^{13}C and ^{1}H chemical shifts. Molecular orbital calculation with geometry optimization has been applied in many investigations as one of the reliable methods for predicting the stable conformer. Among many versions of MO calculation, MNDO[2,3] is known as the most practicable and trustworthy way to estimate the geometry and the energy of conformation of the organic molecule.



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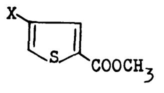

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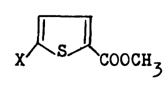

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We will discuss the relation between observed ^{13}C chemical shift and the stable conformers predicted by MNDO calculation. In addition, this report deals with the correlation between the percent *s* character obtained from $^{1}J_{C-H}$ and that calculated by MNDO method.

Experimental

The preparation of materials were described previously.[1] ^{13}C NMR spectra were recorded by a JEOL FX-90Q spectrometer. The concentration of sample solutions was adjusted to approximately 0.6 mol dm^{-3}. The chemical shift was measured in an accuracy of ±0.1 ppm with internal TMS reference in a CDCl$_3$ solution at the probe temperature. Data acquisition was done by the following conditions: flip angle of pulse 30°, number of transients 1000, data points 16384, and spectral width 4500 or 5000 Hz. The ^{13}C–H coupling constant in an accuracy of ±0.1 Hz was obtained from proton coupled spectra measured by the normal gated decoupling technique. Data acquisition was done by the following conditions: flip angle of pulse 45°, number of transients 2000, data points 16384, and spectral width 450 Hz.

MNDO Calculation[2,3]

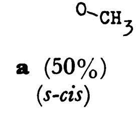
The MNDO (Modified Neglect of Diatomic Overlap) calculation, semiempirical SCF molecular orbital calculation which takes all valence electrons into account, was carried out by MOPAC program[4] on HITACHI M-280H computer at the Computer Center of the University of Tokyo. By the standard MNDO calculation, electronic energy, core-core repulsion energy, ionization potential, heat of formation, density matrix (electron density and bond order), eigenvalue (energy level), and eigenvector of the molecular orbitals can be obtained. The structure of stable conformers of methyl (substituted 2-thiophenecarboxylate)s was estimated by means of XDC data base (Cambridge Crystallographic Data Base) installed at the Computer Center of the University of Tokyo. The structural parameters were used as the input data for the MNDO calculation. The *s* character of the C–H bonds was calculated from the coefficients of the corresponding molecular orbitals.

Results and Discussion

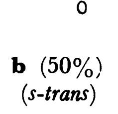
The ^{13}C NMR signals of methyl (3-, 4-, and 5-substituted 2-thiophenecarboxylate)s (**1**—**3**) were assigned by the procedures described below. The signals of protonated carbons were assigned from the coupling constants of carbon-proton bonds. Since $J_{C_5H_5}$ in thiophene compounds is larger than $J_{C_3H_3}$ or $J_{C_4H_4}$ by ca. 15 Hz,[5–7] C_5 and C_4 in the compounds of series **1** and C_5 and C_3 in the compounds **2** are easily distinguished from each other by ^{13}C–H one bond coupling constants. The ^{13}C-signals of C_3 and C_4 in the compounds of series **3** were assigned by the comparison with those of substituted thiophenes and partly by the analysis of line splitting due to a long-range coupling.[5,6] The signals of quaternary carbons were assigned by their intensity, and also by the ^{13}C–H long-range couplings. The results are given in Tables 1—3.

The plots of the chemical shift of carbons in methyl (4-substituted 2-thiophenecarboxylate)s against that of the corresponding carbons in 3-substituted thiophenes[8] showed good linear correlations (δC_2 r[9] 0.917, p 1.09, s 0.396; δC_3 r 0.993, p 1.06, s 0.464; δC_4 r 1.000, p 0.981, s 0.621; δC_5 r 0.996, p 0.898, s 0.843). The chemical shift of carbons in methyl (5-substituted 2-thiophenecarboxylate)s also correlates linearly with that of the corresponding carbons in 2-substituted thiophenes. These results suggest that the additivity rule for the ^{13}C chemical shift of simple substituted thiophenes is applicable to the chemical shift of the ring carbons in methyl (4- and 5-substituted 2-thiophenecarboxylate)s in which two substituents are attached to non-adjacent ring-carbon atoms. However, the chemical shift of carbons in methyl (3-substituted 2-thiophenecarboxylate)s and that of the corresponding carbons in 3-substituted thiophenes showed poor correlations. Thus, the interaction among substituents seems to result in deviation from the linear correlation. The interaction will be of steric nature, and the perturbation by neighboring substituent in a conformational preference can cause a considerable change in chemical shift.

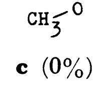
In order to investigate the relation between chemical shift and stable conformation, we have estimated the stable conformation of these thiophene derivatives and their populations by MNDO calculation. Methyl 2-thiophenecarboxylate can take any one of the planar conformers **a**—**d**. Our calculations showed, however, that this ester is a mixture of **a** (50%) and **b** (50%) conformers and that other two conformers (**c** and **d**) have considerably higher energy than **a** and **b**. The calculations also showed that all other esters do not exist in the **c** and **d** conformers. It agrees with



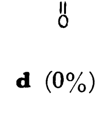
a (50%)
(*s-cis*)



b (50%)
(*s-trans*)



c (0%)



d (0%)

Table 1. ^{13}C NMR Chemical Shifts and ^{13}C–H Coupling Constants of Methyl (3-Substituted 2-Thiophenecarboxylate)s (Series 1)

No.	X	Chemical shifts(δ)								Coupling constants/Hz				
		δ_{C_2}	δ_{C_3}	δ_{C_4}	δ_{C_5}	δ_{CO}	δ_{CH_3}	Others		$J_{C_4H_4}$	$J_{C_5H_5}$	$J_{C_4H_5}$	$J_{C_5H_4}$	Others
1	H	133.8	133.4	127.4	132.4	162.6	52.0			170.3	185.9	3.8	7.0	
2	OCH_3	109.6	162.1	116.4	130.6	162.1	51.4	59.0(OCH_3)		170.4	187.2	3.9	4.3	
3	CH_3	126.7	146.1	131.6	129.9	163.1	51.5	15.8(CH_3))		167.6	185.0	3.7	6.8	4.6($J_{C_4-CH_3}$)
4	Cl	125.9	131.6	130.2	130.4	161.0	52.1			175.9	188.3	3.9	5.8	
5	Br	127.5	117.0	133.0	131.2	161.0	52.1			176.5	188.2	3.8	6.0	
6	I	130.5	86.1	138.6	132.7	161.2	52.1			176.1	187.5	4.1	6.5	
7	CHO	138.5	144.6	127.7	130.6	161.5	52.7	186.3(CHO)		173.9	187.8	4.0	6.8	3.7(J_{C_4-CHO})
8	$COCH_3$	131.2	147.3	128.0	130.9	161.7	52.5	198.4(CO)	30.7(CH_3)	172.0	187.5	4.1	6.5	
9	$COOCH_3$	134.0	137.2	128.7	130.5	161.5	52.5	164.4(CO)	52.6(CH_3)	173.3	188.1	4.1	6.5	
10	NO_2	129.5	148.6	124.1	129.3	159.7	53.3			179.4	192.2	4.1	5.4	

Table 2. ^{13}C NMR Chemical Shifts and ^{13}C–H Coupling Constants of Methyl (4-Substituted 2-Thiophenecarboxylate)s (Series **2**)

No.	X	Chemical shifts(δ)								Coupling constants/Hz				
		δ_{C_2}	δ_{C_3}	δ_{C_4}	δ_{C_5}	δ_{CO}	δ_{CH_3}	Others		$J_{C_3H_3}$	$J_{C_5H_5}$	$J_{C_3H_5}$	$J_{C_5H_3}$	Others
1	H	133.8	133.4	127.4	132.4	162.6	52.0			170.8	185.9	9.0	11.0	
11	OCH_3	132.0	124.3	158.3	105.1	162.4	52.0	57.6(OCH_3)		172.0	184.0	6.6	7.7	
12	CH_3	133.4	135.3	138.4	128.1	162.6	51.9	15.4(CH_3)		167.9	182.4	8.4	10.2	4.2($J_{C_3-CH_3}$) 5.7($J_{C_5-CH_3}$)
13	Cl	134.0	133.0	126.2	126.7	161.5	52.3			176.8	190.3	6.9	8.2	
14	Br	134.6	135.4	110.6	129.5	161.3	52.4			177.3	191.3	7.2	8.7	
15	I	135.4	140.2	77.5	135.2	160.9	52.3			177.2	191.4	7.8	9.6	
16	CHO	135.8	131.2	142.9	140.4	161.7	52.5	184.3(CHO)		174.1	186.5	7.9	9.5	3.0(J_{C_3-CHO})
17	$COCH_3$	134.9	132.5	142.8	137.2	161.9	52.4	191.3(CO)	27.4(CH_3)	173.0	185.9	7.7	9.0	
18	$COOCH_3$	134.6	133.5	134.1	138.0	161.8	52.3	162.3(CO)	52.0(CH_3)	174.9	188.8	7.6	9.2	
19	NO_2	134.9	127.3	148.4	132.1	160.9	52.9			180.8	193.9	6.0	7.4	

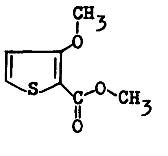
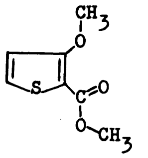
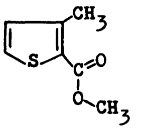
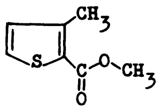
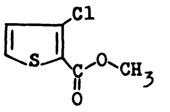
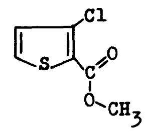
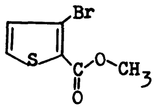
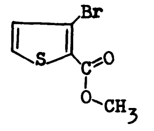
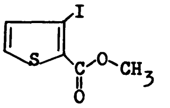
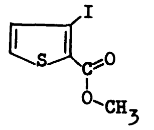
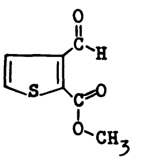
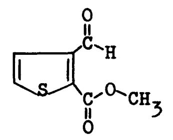
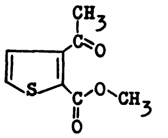
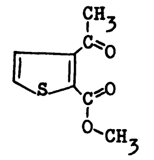
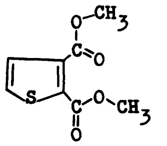
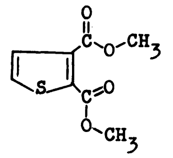
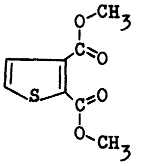
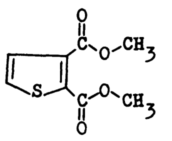
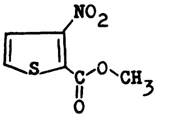
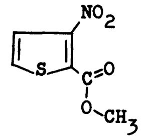
Table 3. ^{13}C NMR Chemical Shifts and ^{13}C–H Coupling Constants of Methyl (5-Substituted 2-Thiophenecarboxylate)s (Series **3**)

No.	X	Chemical shifts(δ)								Coupling constants/Hz				
		δ_{C_2}	δ_{C_3}	δ_{C_4}	δ_{C_5}	δ_{CO}	δ_{CH_3}	Others		$J_{C_3H_3}$	$J_{C_4H_4}$	$J_{C_3H_4}$	$J_{C_4H_3}$	Others
1	H	133.8	133.4	127.4	132.4	162.6	52.0			170.8	170.3	5.5	5.0	
20	OCH_3	118.8	133.2	105.6	172.5	162.8	51.7	60.4(OCH_3)		170.3	169.8	4.0	5.4	
21	CH_3	131.2	133.9	126.4	147.9	162.6	51.8	15.6(CH_3)		170.0	167.8	5.2	4.8	4.2($J_{C_4-CH_3}$)
22	Cl	132.0	133.0	127.3	137.4	161.5	52.2			173.3	174.6	4.3	5.0	
23	Br	134.9	133.6	130.9	120.2	161.4	52.2			173.1	175.0	4.5	5.1	
24	I	139.3	134.3	137.7	82.6	161.1	52.2			172.7	174.7	5.1	5.2	
25	CHO	141.0	133.4	135.0	148.0	161.9	52.7	183.2(CHO)		173.8	170.7	4.6	4.6	
26	$COCH_3$	139.7	133.4	131.6	148.9	162.0	52.5	190.5(CO)	26.9(CH_3)	173.1	170.2	4.5	5.1	
27	$COOCH_3$	139.0	133.0	133.0	139.0	162.0	52.5	162.0(CO)	52.5(CH_3)	173.0	173.0	4.9	4.9	
28	NO_2	138.5	131.7	128.0	155.5	161.0	53.0			176.7	178.1	3.6	4.8	

the previous reports informing the predominance of (*Z*)-conformations in alkoxycarbonyl groups.10–12)

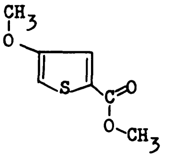
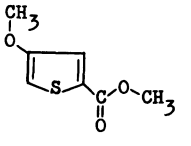
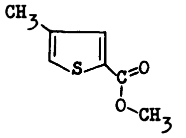
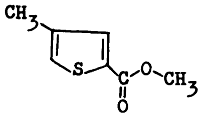
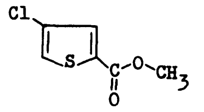
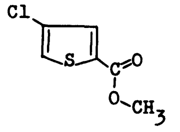
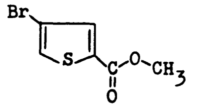
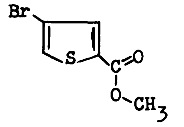
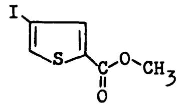
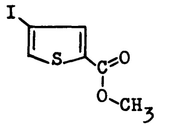
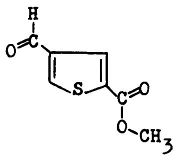
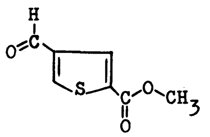
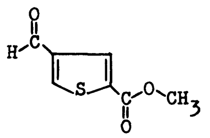
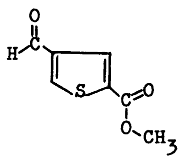
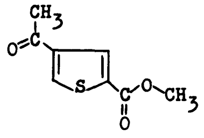
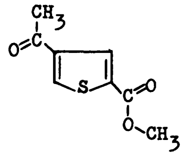
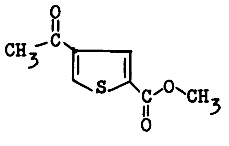
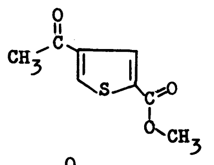
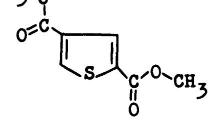
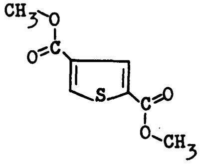
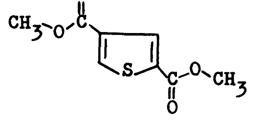
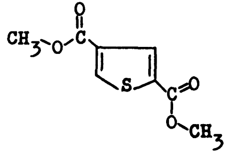
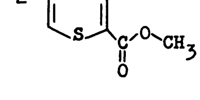
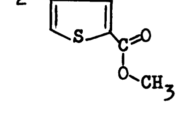
In general, conjugated enones take *s-trans* (**b**) conformation preferentially, while the electrostatic interaction between sulfur and carbonyl dipole repels to each other to make the *s-cis* (**a**) conformer

Table 4. The Stable Conformers and Their Abundance (%) of Methyl (3-Substituted 2-Thiophenecarboxylate)s (Series **2**)

Conformer	Abundance %	Conformer	Abundance %	Conformer	Abundance %	Conformer	Abundance %
	75		25				
	61		38				
	69		31				
	68		32				
	62		38				
	76		24				
	81		19				
	51		28		14		7
	71		29				

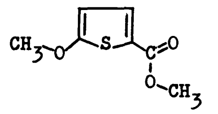
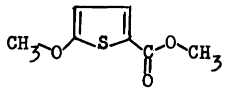
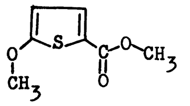
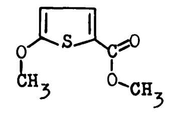
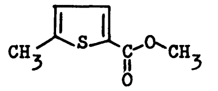
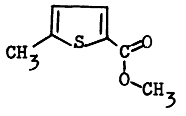
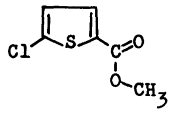
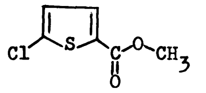
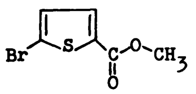
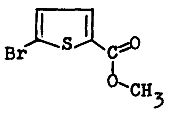
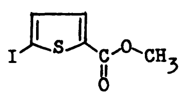
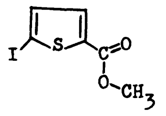
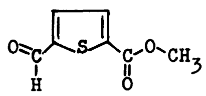
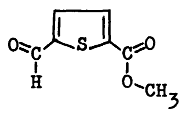
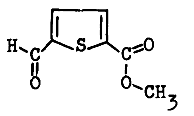
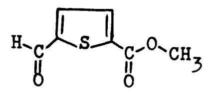
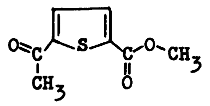
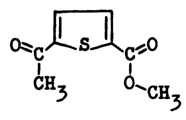
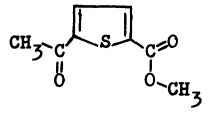
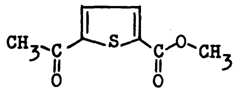
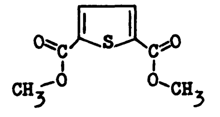
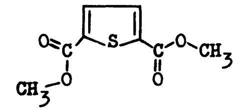
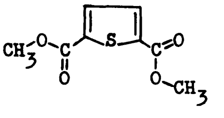
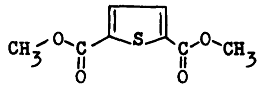
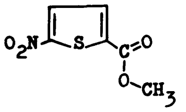
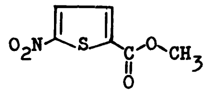
predominant. Thus, the competition of effects of opposite directions controls the equilibrium between the conformers. The stable conformations calculated and their populations for methyl (substituted 2-thiophenecarboxylate)s are shown in Tables 4—6. The two possible rotamers about the methoxycarbonyl group of methyl (4- and 5-substituted 2-thiophenecarboxylate)s are estimated to be nearly

Table 5. The Stable Conformers and Their Abundance (%) of Methyl (4-Substituted 2-Thiophenecarboxylate)s (Series **2**)

Conformer	Abundance %	Conformer	Abundance %	Conformer	Abundance %	Conformer	Abundance %
	54		46				
	50		50				
	57		43				
	56		44				
	55		45				
	44		43		9		4
	51		33		11		5
	45		31		17		7
	66		34				

equally populated, because the energy difference between *s-cis* and *s-trans* conformers calculated is small, though the *trans* conformer has a slightly lower energy than the *cis* conformer. This implies that the conformational distribution of these substituted compounds is similar to that of parent methyl 2-thiophenecarboxylate, and, in addition, the four stable conformers exist in a nearly equal population even when the substituent (X) is unsymmetrical with respect to the plane perpendicular to molecular plane

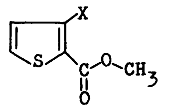
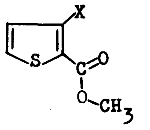
Table 6. The Stable Conformers and Their Abundance (%) of Methyl (5-Substituted 2-Thiophenecarboxylate)s (Series **3**)

Conformer	Abundance %	Conformer	Abundance %	Conformer	Abundance %	Conformer	Abundance %
	31		28		21		20
	51		49				
	50		50				
	50		50				
	51		49				
	30		26		23		21
	38		31		17		14
	27		26		26		23
	51		49				

(i.e. when the substituent is methyl, formyl, acetyl, and methoxycarbonyl). In methyl (4- and 5-substituted 2-thiophenecarboxylate)s, methoxycarbonyl group was confirmed to be coplanar with thiophene ring. The additivity rule for the ^{13}C chemical shift of substituted thiophenes should be applicable to explain the chemical shift of ring carbons in the compounds of series of **2** and **3**, because the effect of two dissimilar conformations balances in series **2** and **3**.

In the compounds of series **1**, the conformational equilibrium tends to shift to the most stable conformer, and the population sometimes becomes as high as 80%, generally ca. 70%. As a whole, the neighboring substituent effect seems to be governed by the electrostatic interaction between substituent and 2-methoxycarbonyl group, as revealed by calculated dipole moments of conformers (Table 7). As enone is inclined to take the electrostatically stabilized *s-trans* conformation, *s-trans* conformers of **1** predominate over other conformers. In other words, carbonyl group of 2-methoxycarbonyl tends to lie *anti* to the

Table 7. Calculated Dipole Moments and Populations of the Most and Next Stable Conformers of **1**

X				
	Dipole moment/D	Population %	Dipole moment/D	Population %
H	2.58	50	1.65	50
Cl	1.79	69	2.48	31
Br	1.81	68	2.24	32
I	1.66	62	2.25	38
NO_2	2.77	71	5.22	29
CH_3	2.62	38	1.50	62
CH_3CO (*s-cis*)	3.46	81	3.51	19
CHO (*s-trans*)	0.36	24	2.76	76*

a) This conformer is capable of forming CH···O hydrogen bond.

Table 8. Electron Density of Methyl (Substituted 2-Thiophenecarboxylate)s

No.	X	e_{S_1}	e_{C_2}	e_{C_3}	e_{C_4}	e_{C_5}	e_{CO}	e_{CH_3}	Others
				3-Substituted compounds					
1	H	0.157	−0.212	0.014	−0.111	−0.119	0.397	0.187	
2	OCH_3	0.181	−0.250	0.157	−0.160	−0.095	0.406	0.187	0.182(OCH_3)
3	CH_3	0.153	−0.198	−0.027	−0.095	−0.119	0.396	0.187	0.079(CH_3)
4	Cl	0.187	−0.196	0.047	−0.094	−0.118	0.395	0.186	
5	Br	0.185	−0.181	−0.012	−0.086	−0.111	0.354	0.186	
6	I	0.179	−0.162	−0.157	−0.079	−0.122	0.388	0.186	
7	CHO	0.164	−0.159	−0.100	−0.064	−0.127	0.392	0.186	0.305(CHO)
8	$COCH_3$	0.184	−0.131	−0.081	−0.083	−0.128	0.382	0.185	0.231(CO) 0.006(CH_3)
9	$COOCH_3$	0.179	−0.134	−0.049	−0.067	−0.134	0.381	0.185	0.370(CO) 0.186(CH_3)
10	NO_2	0.220	−0.121	−0.033	−0.059	−0.130	0.378	0.184	
				4-Substituted compounds					
11	OCH_3	0.173	−0.196	−0.017	0.036	−0.146	0.396	0.187	0.188(OCH_3)
12	CH_3	0.157	−0.212	0.030	−0.155	−0.101	0.397	0.187	0.093(CH_3)
13	Cl	0.184	−0.207	0.026	−0.065	−0.102	0.396	0.186	
14	Br	0.182	−0.210	0.032	−0.123	−0.087	0.397	0.187	
15	I	0.178	−0.210	0.041	−0.268	−0.068	0.397	0.187	
16	CHO	0.172	−0.215	0.044	−0.231	−0.038	0.397	0.187	0.324(CHO)
17	$COCH_3$	0.177	−0.215	0.038	−0.192	−0.039	0.396	0.187	0.259(CO) 0.002(CH_3)
18	$COOCH_3$	0.180	−0.220	0.050	−0.157	−0.036	0.397	0.187	0.384(CO) 0.187(CH_3)
19	NO_2	0.219	−0.212	0.051	−0.137	−0.028	0.397	0.187	
				5-Substituted compounds					
20	OCH_3	0.178	−0.242	0.051	−0.181	0.030	0.401	0.188	0.178(OCH_3)
21	CH_3	0.169	−0.211	0.012	−0.092	−0.162	0.396	0.187	0.088(CH_3)
22	Cl	0.206	−0.208	0.013	−0.080	−0.098	0.396	0.187	
23	Br	0.209	−0.206	0.009	−0.069	−0.154	0.395	0.187	
24	I	0.207	−0.200	−0.006	−0.047	−0.296	0.394	0.187	
25	CHO	0.213	−0.190	−0.009	−0.030	−0.252	0.393	0.187	0.323(CHO)
26	$COCH_3$	0.188	−0.185	−0.010	−0.018	−0.209	0.392	0.187	0.258(CO) 0.002(CH_3)
27	$COOCH_3$	0.227	−0.195	−0.013	−0.013	−0.195	0.400	0.190	
28	NO_2	0.276	−0.174	−0.020	0.018	−0.197	0.389	0.186	

electronegative group at the 3-position, avoiding close access of two negatively charged atoms. Exceptionally, in methyl 3-formyl-2-thiophenecarboxylate, the *s-cis* conformer which has higher dipole moment is predominant to the *trans* conformer. In the most stable conformer of the formyl derivative, weak intramolecular interaction like hydrogen bonding[13] will occur between formyl proton and carbonyl oxygen of methoxycarbonyl group, because the proton is acidic due to the electron-attracting ability of formyl carbonyl oxygen. The assumption is supported by remarkably large bond population (0.00338) between nonbonded formyl hydrogen and carbonyl oxygen of 2-$COOCH_3$. The bond population between two nonbonded atoms is usually less than 10^{-5}. In respect of this figure, the bond population is exceptionally large and comparable to the value for $OH\cdots\pi$ hydrogen bonded atoms.[14] On the other hand, in acetyl, methoxycarbonyl, and nitro derivatives, methoxycarbonyl group will lose the coplanarity with thiophene ring due to the steric hindrance. Since the alkoxycarbonyl conformation of 3-substituted 2-thiophenecarboxylates is remarkably altered by a neighboring substituent, the magnetic anisotropy and electric field by carbonyl group will affect differently the chemical shift of ring carbons in each compound.[15] The chemical shift of ring carbons of methyl (3-substituted 2-thiophenecarboxylate)s is not correlated linearly with that of substituted thiophenes. However, if various effects by steric and electronic interactions between the neighboring substituents on thiophene ring in the compounds of series **1** are corrected, the ^{13}C chemical shift of compounds of this series will be correlated well with those of substituted thiophenes.

The electron density values derived from MNDO calculation of methyl (substituted 2-thiophenecarboxylate)s are summarized in Table 8. Levy and coworkers have reported that the plot of ^{13}C chemical shift vs. CNDO/2 total charge density for para position of substituted benzene shows fairly good linearity.[16] However, the MNDO electron density on the C_2 of compounds of series **3** which corresponds to *para* position in substituted benzene[17,18] correlates poorly with the ^{13}C chemical shift. For all the compounds studied, plots of the electron density against ^{13}C chemical shift showed poor correlations. As the electron density in MNDO calculation is of the diamagnetic term, the ^{13}C chemical shift in methyl (substituted 2-thiophenecarboxylate)s is considered to be controlled by the paramagnetic contributions as the case of pyridine.[19]

The ^{13}C–H one bond coupling constant of the ring C–H of methyl (substituted 2-thiophenecarboxylate)s is correlated linearly with that of substituted thiophenes [${}^1J_{C_4H_4}$ (**1**) r 0.991, p 0.903, s 0.465; ${}^1J_{C_5H_5}$ (**1**) r 0.975, p 1.04, s 0.442; ${}^1J_{C_3H_3}$ (**2**) r 0.996, p 0.958, s 0.364; ${}^1J_{C_5H_5}$ (**2**) r 0.999, p 0.973, s 0.192; ${}^1J_{C_3H_3}$ (**3**) r 0.990, p 0.854, s 0.301; ${}^1J_{C_4H_4}$ (**3**) r 0.994, p 0.899, s 0.297]. It is interesting that the relation between the ^{13}C–H one bond coupling constants of methyl (3-substituted 2-thiophenecarboxylate)s and those of 3-substituted thiophenes is linear. Although the substituent effect on the ^{13}C chemical shift of ring carbons is considerably affected by steric and electronic interactions between neighboring substituents, the substituent effect on ${}^1J_{C_4H_4}$ (**1**) and ${}^1J_{C_5H_5}$ (**1**) is linear.

Table 9. Comparison of Observed and Calculated Persent *s* Characters of C–H Bonds for Methyl (Substituted 2-Thiophenecarboxylate)s

No.	X	$\rho_{C_3H_3}$(%)		$\rho_{C_4H_4}$(%)		$\rho_{C_5H_5}$(%)	
		obs	calcd	obs	calcd	obs	calcd
		3-Substituted compounds					
1	H	—	—	34.1	33.5	37.2	36.0
2	OCH_3	—	—	34.1	33.4	37.4	36.0
3	CH_3	—	—	33.5	33.7	37.0	36.0
4	Cl	—	—	35.2	33.8	37.7	36.2
5	Br	—	—	35.3	33.8	37.6	36.2
6	I	—	—	35.2	33.9	37.5	36.2
7	CHO	—	—	34.8	34.0	37.6	36.2
8	$COCH_3$	—	—	34.4	33.6	37.5	36.1
9	$COOCH_3$	—	—	34.7	33.9	37.6	36.1
10	NO_2	—	—	35.9	34.1	38.4	36.4
		4-Substituted compounds					
11	OCH_3	34.4	33.5	—	—	36.8	35.9
12	CH_3	33.6	33.6	—	—	36.5	36.1
13	Cl	35.4	33.8	—	—	38.1	36.2
14	Br	35.5	33.9	—	—	38.3	36.2
15	I	35.4	33.9	—	—	38.3	36.3
16	CHO	34.8	33.7	—	—	37.3	36.3
17	$COCH_3$	34.6	33.6	—	—	37.2	36.3
18	$COOCH_3$	35.0	33.9	—	—	37.8	36.3
19	NO_2	36.2	34.1	—	—	38.8	36.2
		5-Substituted compounds					
20	OCH_3	34.1	33.8	34.0	33.6	—	—
21	CH_3	34.0	33.5	33.6	33.6	—	—
22	Cl	34.7	33.8	34.9	33.8	—	—
23	Br	34.6	33.7	35.0	33.7	—	—
24	I	34.5	33.7	34.9	33.8	—	—
25	CHO	34.8	33.7	34.1	33.9	—	—
26	$COCH_3$	34.6	33.7	34.0	33.8	—	—
27	$COOCH_3$	34.6	33.7	34.6	33.7	—	—
28	NO_2	35.3	34.0	35.6	33.9	—	—

The percent s character (ρ_{C-H}) obtained by an empirical correlation expressed by Eq. 1[20] from ${}^1J_{C-H}$ of methyl (substituted 2-thiophenecarboxylate)s is given in Table 9 together with the results calculated by MNDO method.

$$\rho_{C-H} = 0.2\,{}^1J_{C-H} \qquad (1)$$

It was shown in Tables 1 and 2 that ${}^1J_{C_5H_5}$ is larger than

$^{1}J_{C_3H_3}$ or $^{1}J_{C_4H_4}$, and the same tendency also appeared in the results by MNDO calculation. Plots of the percent *s* characters for all 28 compounds from $^{1}J_{C-H}$ and MNDO method showed a good correlation (r 0.940, p 0.718, s 0.386).

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14) Respective non-bonded OH···C bond populations in the CH···π hydrogen-bonded conformers (two species) of 1-phenyl-2-propanol were reported to be 4.79×10^{-3} and 7.44×10^{-3}. See: K. Abe, M. Hirota, and K. Morokuma, *Bull. Chem. Soc. Jpn.*, **58**, 2713 (1985).

15) For example, the differences between the observed and the calculated ^{13}C chemical shifts of methyl 3-formyl-2-thiophenecarboxylate were 6.8, 5.1, 1.8, and 4.1 ppm, on C_2, C_3, C_4, and C_5, respectively. The differences on C_3 and C_5 are explained by the change of conformation of methoxycarbonyl group, because the differences in electron density (Δe) between the two conformers of methyl 3-formyl-2-thiophenecarboxylate become in the order $C_3(0.013>C_5(0.007)>C_2(0.002), C_4(0.002)$. The 3-formyl group is fixed to take the (E) conformation with respect to the C_3–C_{formyl} bond in methyl 3-formyl-2-thiophenecarboxylate, while 3-thiophenecarbaldehyde exists as a mixture of the two possible conformers. Thus, the reference chemical shift value of 3-thiophenecarbaldehyde corresponds to the equilibrium mixture of the conformers, and the difference in electron density on C_2 of the two conformers (Δe=0.029) may cause large deviation. Accordingly, it is considered that the chemical shift of β-carbon to carbonyl group changes more than 5 ppm by complete change of the carbonyl conformation.

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