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The C-13 NMR Spectra of Thiophenes. II. 2-Substituted Thiophenes

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Synopsis. Carbon-13 NMR data of 14 2-substituted thiophenes were obtained in $CDCl_3$. The correlation between the carbon chemical shifts and the Hammet constants was poor. The charge densities of typical compounds were calculated by the CNDO/2 method and they discussed in connection with the observed C-13 chemical shifts.

As an extension of our NMR studies of substituted thiophenes,[1–3] we have measured the C-13 NMR spectra of 14 2-substituted thiophenes and compared the data with those of the corresponding benzene derivatives.

Experimental

The C-13 NMR spectra were measured in a moderately concentrated solution (50 mg/0.8 ml) in $CDCl_3$ using a Varian XL-200 spectrometer with a frequency of 50.3 MHz. The chemical shifts were referred to an internal TMS signal. The compounds examined were prepared according to the methods previously reported in the literature. The chemical shifts and the coupling constants were obtained by the first-order analyses.

Results and Discussion

The C-13 chemical shifts and the one-bond carbon-proton coupling constants observed are tabulated in Tables 1 and 2, in which the values for monosubstituted benzenes, measured at a similar concentration (50 mg/0.8 ml) in $CDCl_3$, are also included for the sake of comparison. The values in Table 1 are almost entirely consistent with previously reported values in a pure liquid[1,2] and in an acetone solution.[4]

As may be seen in Table 1, the C_2 chemical-shift range (94 ppm) is rather wide as compared with those of the C_3 (34 ppm), the C_4 (5), and the C_5 (24). This indicates that, besides the inductive effect, the magnetic anisotropy effect of the substituent considerably affects the C_2 chemical shift, as has been pointed out previously for the monosubstituted benzenes.[5] The C_2, C_3, C_4, and C_5 shifts show parallel correlations with those of the C_{ipso}, C_o, C_m, and C_p of the corresponding monosubstituted benzenes respectively. The relation can be expressed by a simple equation as follows:

$$\delta(\mathrm{T}) = a \cdot \delta(\mathrm{B}) + b,$$

where δ(T) is a C-13 chemical shift of a thiophene derivative and δ(B) is that of the corresponding benzene. The correlation coefficients are 0.981, 0.871, and 0.935, and the proportional coefficients (a) are about 1.40, 1.62, and 1.42 for the C_2, C_3, and C_5 shifts respectively. Among the three, the C_3 shifts have the lowest correlation coefficient, because they suffer the so-called ortho-effect from their substituents. The C_5 shifts have a better correlation with the C_p shifts, for which the change was interpreted by the resonance effect of the substituents.[5] The C_4 shifts change little with the substituents and have no linear relation with the corresponding C_m shifts.

The electron densities of the carbons in the thiophenes have been calculated by the CNDO/2 method with or without d-orbitals.[6] The geometry of the thiophene skeleton was taken from a microwave geometry,[7] while those of the substituents were assumed to be the standard ones described previously.[8] Two planar geometries are considered in such

Table 1. ^{13}C NMR Chemical shifts of 2-substituted thiophenes and monosubstituted benzenes in ppm relative to tetramethylsilane in $CDCl_3$ at 50.3 MHz[a]

No.	Substituent	Thiophenes					Benzenes				
		C_2	C_3	C_4	C_5	Others	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	Others
1	CHO	144.06	136.28	128.33	135.09	182.95	136.42	129.76	129.00	134.47	192.44
2	CH_3CO	144.60	132.46	128.11	133.75	26.91 190.68	137.16	128.57	128.30	133.09	26.58 198.09
3	I	73.06	136.86	128.83	131.45		94.35	134.46	130.21	127.42	
4	CO_2CH_3	133.62	133.46	127.73	132.33	52.13 162.68	130.22	129.59	128.37	132.90	52.07 167.11
5	CN	109.91	137.41	127.67	132.60	114.22	112.47	132.14	129.13	132.78	118.83
6	NO_2	152.51[b]	128.58	127.02	132.56		148.24	123.48	129.31	134.58	
7	Br	112.14	129.81	127.61	126.95		122.51	131.53	130.01	126.85	
8	H	125.10	126.85	126.85	125.10		128.33	128.33	128.33	128.33	
9	Cl	130.05	126.05	126.60	124.07		134.28	128.62	129.70	126.42	
10	CH_3	139.59	125.11	126.87	123.02	15.04	137.86	129.05	128.25	125.32	21.44
11	C_2H_5	147.38	123.24	126.66	122.63	16.05 23.27	144.25	128.29	127.85	125.57	15.61 28.88
12	OCH_3	166.71	103.75	124.71	111.74	60.37	159.56	113.90	129.43	120.64	55.09
13	$NHCOCH_3$	138.96	111.94	123.87	118.04	23.24 166.72	138.08	120.19	128.89	124.28	24.37 169.01
14	SO_2Cl	144.03	135.83	127.78	134.91		144.44	126.99	129.71	135.25	

a) Errors are estimated to be ±0.03 ppm. b) The value was obtained in a more concentrated solution (172 mg/0.8 ml).

Table 3. CNDO/2 Calculated total charge densities on the carbons of 2-substituted thiophenes ($\times 10^3$)[a)]

No.	Without d orbitals				With d orbitals			
	C_2	C_3	C_4	C_5	C_2	C_3	C_4	C_5
1	−11 (−8)	+14 (+24)	−18 (−21)	+17 (+23)	−43 (−40)	+51 (+62)	+31 (+28)	−27 (−21)
2	−16 (−13)	+10 (+22)	−18 (−20)	+16 (+22)	−46 (−46)	+48 (+60)	+31 (+28)	−29 (−21)
5	+38	+0	−12	+10	+9	+42	+37	−34
6	+8 (+23)	+33 (+12)	−15 (−4)	+26 (+13)	−19 (−5)	+67 (+52)	+36 (+45)	−19 (−29)
8	+5	−9	−9	+5	−36	+38	+38	−36
9	+20	−36	+1	−2	+41	+48	+37	−32
10	+55	−36	−4	−3	+18	+9	+44	−45
12	+193 (+197)	−97 (−85)	+13 (+10)	−19 (−14)	+156 (+156)	−50 (−41)	+64 (+59)	−60 (−55)

a) The value in parentheses is that calculated in another planar geometry (see text) except in the case of **6**, in which the plane of the substituent group is taken as perpendicular to the molecular plane. The values are given in units of the absolute value of the charge of an electron.

Table 2. The coupling constants between carbon-13 and directly bonded protons in thiophenes in Hz[a)]

No.	$^1J(C_3H_3)$	$^1J(C_4H_4)$	$^1J(C_5H_5)$
1	168	171	186
2	168	170	185
3	172	169	187
4	171	169	183
5	173	172	187
6	176	173	187
7	173	171	188
8	168	168	186
9	172	170	189
10	165	167	185
11	165	166	186
12	167	168	189
14	176	174	187

a) Errors are estimated to be ±1.3 Hz.

cases as **2** where the orientation of the conjugated substituent can be in two ways on a molecular plane. Therefore, the results are shown by several sticks in Fig. 1 and are given in Table 3. The two ends of the stick in Fig. 1 correspond to the charge densities of the C_5 with two substituent orientations. Thus, the length of the stick shows the variation in the charge density dependent upon the conformation of the substituent. The proportionality coefficient of the C_5 shifts *vs.* their total charge densities is deduced to be −604 ppm/electron from Fig. 1 (r=0.93). As can be seen in Table 3, our calculation shows that the total charge densities increase at the C_α carbons and decrease at the C_β carbons when the d-orbitals are included in the calculation. Recently Osamura *et al.* pointed out the importance of the vacant d-orbitals of the sulfur atom.[9)]

As we have described before,[1)] the correlation between the C_5 shifts and the Hammet constants σ_p is not very good (r=0.85). The correlation with σ_p^+ seems to be better (r=0.90) than that with σ_p.[10)]

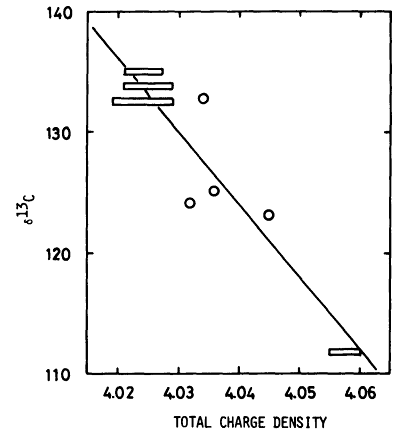

Fig. 1. Plot of C-13 chemical shifts in ppm (ordinate) *vs.* total charge densities (abscissa) for the C_5 of 2-substituted thiophenes.

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