NMR Spectra of Substituted 2-(2-Nitrovinyl)thiophenes

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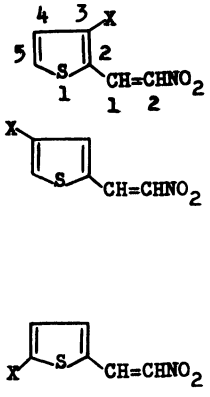
Synopsis. ^{1}H and ^{13}C NMR spectra are reported for substituted 2-(2-nitrovinyl) thiophenes. The proton chemical shifts and coupling constants were correlated closely with those of methyl *trans*-3-(5-substituted 2-thienyl) acrylates. We have found that the additivity rule for ^{13}C chemical shifts of simple substituted thiophenes is applicable to the shifts of the ring carbons in substituted 2-(2-nitrovinyl) thiophenes.

The antibacterial property of 2-(2-nitrovinyl) thiophene has been well known.[1] Recently, we also reported some new antibacterial and fungicidal (nitrovinyl) thiophenes.[2]

We examined the substituent effect in ^{1}H and ^{13}C NMR spectra of a series of substituted 2-(2-nitrovinyl) thiophenes.



	X=H	1
	X=CH_3	2
	X=Br	3
	X=OCH_3	4
	X=Cl	5
	X=Br	6
	X=I	7
	X=OCH_3	8
	X=CH_3	9
	X=Cl	10
	X=Br	11
	X=I	12
	X=CHO	13
	X=$COCH_3$	14
	X=COOH	15
	X=$COOCH_3$	16
	X=NO_2	17
	X=CH=$CHNO_2$	18

^{1}H NMR spectra of substituted (2-nitrovinyl) thiophenes are very similar to those of methyl *trans*-3-(substituted 2-thienyl)acrylate.[3] Thus, assignment was made easily by comparing the spectra of two series of the compounds. The results are given in Table 1. The chemical shifts of protons in 5-substituted 2-(2-nitrovinyl)thiophenes (X=H, OCH_3, CH_3, Cl, Br, I, CHO, $COCH_3$, $COOCH_3$, and NO_2) against those of the corresponding protons in methyl *trans*-3-(5-substituted 2-thienyl)acrylates give good linear correlations [$\delta H(3)$[3] r 0.963, p 0.970, s 0.038; $\delta H(4)$ r 0.992, p 0.963, s 0.062: $\delta H(\alpha)$[4] r 0.726, p 0.726, s 0.121; and $\delta H(\beta)$ r 0.959, p 1.05, s, 0.048], where r designates correlation coefficient, p slope, and s standard deviation.

^{13}C NMR chemical shifts (Table 2) were assigned as described below. C(β) substituted by NO_2 was unambiguously identified by its broad line width and lower intensity. The quaternary ring carbons were identified by lower intensity. C(2) and another carbon carrying the substituent were assigned on the basis of the substituent effect on substituted thiophenes.[5,6] The protonated carbons were assigned in comparison with the coupling constants between coarbons and protons. C(α) was easily identified by the smallest one bond coupling in the protonated carbons. C(3) and C(4) in 5-substituted 2-(2-nitrovinyl) thiophenes were assigned on the basis of the long-range couplings with H(α), because C(3) couples considerably with H(α), but C(4) does not.

Good linear correlations were obtained between the ^{13}C chemical shifts of the ring in substituted 2-(2-nitrovinyl) thiophenes and the corresponding chemical shifts in substituted thiophenes[6] [$\delta C(2)$ r 0.988, p 0.909, s 0.793; $\delta C(3)$ r 0.944, p 0.900, s 1.77; $\delta C(4)$ r 0.997, p 1.01, s 1.15; and $\delta C(5)$ r 0.998, p 0.945, s 1.30]. These results suggest that the additivity rule for ^{13}C chemical shifts of simple substituted thiophenes is

TABLE 1. ^{1}H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF SUBSTITUTED 2-(2-NITROVINYL)THIOPHENES

Compounds	Chemical shifts (δ)						Coupling constants/Hz								
	H(3)	H(4)	H(5)	H(α)	H(β)	Others	J_{34}	J_{35}	J_{45}	$J_{\alpha\beta}$	$J_{3\alpha}$	$J_{5\alpha}$	$J_{3\beta}$	$J_{5\beta}$	Others
1	7.76	7.25	7.85	8.26	7.77		3.7	1.2	5.1	13.5	0.5	0.6	0.4	0.4	
2	—	7.09	7.72	8.26	7.62	2.46(CH_3)	—	—	4.9	13.5	—	0.5	—	0.4	0.4(J_{CH_3-4}) 0.4(J_{CH_3-5})
3	—	7.30	7.93	8.15	7.88		—	—	5.4	13.5	—	0.6	—	0.4	
4	7.41	—	6.90	8.11	7.75	3.85(OCH_3)	—	1.8	—	13.4	0.5	0.5	0.4	0.4	
5	7.72	—	7.76	8.20	7.87		—	1.5	—	13.4	0.5	0.6	0.4	0.4	
6	7.75	—	7.87	8.22	7.86		—	1.5	—	13.5	0.5	0.6	0.5	0.4	
7	7.80	—	7.99	8.24	7.84		—	1.3	—	13.5	0.5	0.6	0.5	0.4	
8	7.50	6.47	—	8.15	7.49	4.04(OCH_3)	4.2	—	—	13.2	0.5	—	0.4	—	
9	7.56	6.95	—	8.18	7.62	2.56(CH_3)	3.7	—	—	13.2	0.5	—	0.4	—	0.5(J_{CH_3-3}) 0.9(J_{CH_3-4})
10	7.64	7.20	—	8.19	7.75		4.0	—	—	13.4	0.5	—	0.4	—	
11	7.59	7.32	—	8.21	7.77		4.0	—	—	13.4	0.5	—	0.4	—	
12	7.45	7.48	—	8.23	7.75		3.9	—	—	13.5	0.5	—	0.4	—	
13	7.89	8.04	—	8.31	7.99	10.04(CHO)	4.0	—	—	13.5	0.6	—	0.4	—	
14	7.81	7.91	—	8.26	7.93	2.60($COCH_3$)	4.0	—	—	13.5	0.6	—	0.4	—	
15	7.79	7.81	—	8.27	7.93	5.99(COOH)	4.0	—	—	13.6	0.6	—	0.4	—	
16	7.79	7.82	—	8.27	7.94	3.91($COOCH_3$)	4.0	—	—	13.6	0.6	—	0.4	—	
17	7.82	8.10	—	8.27	8.09		4.4	—	—	13.5	0.6	—	0.4	—	
18	7.84	7.84	—	8.28	7.88		—	—	—	13.5	0.6	—	0.4	—	

TABLE 2. ^{13}C NMR CHEMICAL SHIFTS OF SUBSTITUTED 2-(2-NITROVINYL)THIOPHENES

Compounds	Chemical shifts (δ)						
	C(2)	C(3)	C(4)	C(5)	C(α)	C(β)	Others
1	134.7	135.6	129.7	132.9	132.7	136.4	
2	128.9	147.1	132.7	131.4	131.2	135.5	14.4(CH_3)
3	129.7	120.3	132.9	133.0	130.2	137.8	
4	133.0	125.5	160.3	105.3	132.7	136.6	58.0(OCH_3)
5	135.4	133.8	127.3	127.2	131.5	137.8	
6	136.1	136.3	111.9	129.9	131.3	137.8	
7	136.8	141.5	79.4	135.7	131.0	137.7	
8	121.1	137.8	107.3	173.3	134.4	133.0	61.3(OCH_3)
9	132.8	137.0	128.6	148.8	133.1	135.3	15.7(CH_3)
10	133.9	135.7	129.4	136.4	132.0	136.7	
11	136.7	136.4	133.1	119.4	131.7	136.9	
12	140.9	137.1	140.0	82.8	131.2	137.1	
13	142.2	135.4	137.8	148.1	131.8	139.6	181.4(CHO)
14	141.2	135.5	134.2	149.1	131.9	139.0	26.8($COCH_3$) 191.0($COCH_3$)
15	140.3	135.0	134.9	139.6	131.9	138.7	162.4(COOH)
16	140.5	134.9	134.9	138.6	131.8	138.9	52.9($COOCH_3$) 162.2($COOCH_3$)
17	140.9	133.5	130.4	155.1	131.1	140.4	
18	139.7	136.2	136.2	139.7	131.6	138.6	

TABLE 3. MELTING POINTS AND ANALYTICAL DATA OF NEW 2-(2-NITROVINYL)THIOPHENES

Compounds	Mp/θ_m/°C	Formula	Found (%)				Calcd (%)			
			C	H	N	S	C	H	N	S
4	118	$C_7H_7NO_3S$	45.30	3.82	7.70	17.40	45.40	3.81	7.56	17.31
5	118	$C_6H_4ClNO_2S$	38.18	2.09	7.26	16.98	38.01	2.13	7.39	16.91
7	106	$C_6H_4INO_2S$	25.50	1.49	5.07	11.52	25.64	1.43	4.98	11.41
8	129	$C_7H_7NO_3S$	45.33	3.85	7.43	17.43	45.40	3.81	7.56	17.31
12	138	$C_6H_4INO_2S$	25.73	1.52	4.85	11.59	25.64	1.43	4.98	11.41
14	154	$C_8H_7NO_3S$	48.79	3.51	7.02	16.32	48.72	3.58	7.10	16.26
15	199(dec)	$C_7H_5NO_4S$	42.05	2.63	7.00	16.17	42.21	2.53	7.03	16.10
16	173	$C_8H_7NO_4S$	45.28	3.20	6.51	15.18	45.07	3.31	6.57	15.04
18	197(dec)	$C_8H_6N_2O_4S$	42.57	2.76	12.49	14.02	42.48	2.67	12.38	14.17

applicable to the shifts of the ring carbons in substituted 2-(2-nitrovinyl)thiophenes.

Chemical shifts of the ring carbons are not always correlated closely with those of hydrogen atoms attached to them. In all the compounds stuidied, $\delta H(\alpha)$ appeared at considerably lower field than $\delta H(\beta)$. In contrast, $\delta C(\alpha)$ appeared at higher field than $\delta C(\beta)$, except for **8**. The substituent effect of methoxy group may be transmitted more strongly by the contribution of resonance structures to $\delta C(\beta)$ in **8**, as to $\delta H(\beta)$ in methyl *trans*-3-(5-methoxy 2-thienyl)acrylate.[3] In 4-substituted compounds, $\delta H(3)$ appeared at lower field than $\delta H(5)$, but $\delta C(3)$ at higher field than $\delta C(5)$. These facts can be a reason for the poor correlations between δH and δC. It is exceptional that plot of $\delta H(\beta)$ *vs.* $\delta C(\beta)$ gave a good correlation (r 0.985, p 11.9, s 0.315). Besides, $\delta C(\beta)$ of 5-substituted compounds (X=H, OCH_3, CH_3, Cl, Br, I, CHO, $COCH_3$, $COOCH_3$, and NO_2) against Hammett's σ_p value[7,8] gave a good correlation (r 0.900, p 6.43, s 8.90). The effect of the substituent on the 5-position may be transmitted more regularly to $\delta H(\beta)$ and $\delta C(\beta)$ than others as observed with methyl *trans*-3-(5-substituted 2-thienyl)acrylates.[3]

Experimental

^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. ^1H(±0.01 ppm) and ^{13}C(±0.1 ppm) chemical shifts were measured from internal TMS reference in $(CD_3)_2CO$ solution at probe temperature. ^1H spectra were obtained, using 45° pulse flip angle and 900 or 1100 Hz spectra width and proton decoupled ^{13}C spectra, using 30° pulse flip angle and 4500 or 5000 Hz spectra width. Proton coupled ^{13}C spectra were obtained by the normal gate decoupling technique in $(CD_3)_2SO$ solution.

Thiophenes (**1**, **2**, **3**, **6**, **9**, **10**, **11**, **13**, and **17**) were prepared according to the reported methods.[1,9-10] Melting points and analytical data of new compounds are given in Table 3.

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