

A CORRELATION BETWEEN PROTON COUPLING CONSTANTS AND SUBSTITUENT ELECTRONEGATIVITY IN 2-SUBSTITUTED THIOPHENES

M. J. BULMAN

Department of Chemistry, The University, Southampton

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Abstract—The NMR spectra of a series of thiophenes with 2-substituents ranging in electronegativity from lithium to fluorine have been analysed accurately, and the three proton-proton coupling constants found to vary linearly with the electronegativity of the substituents. The correlations are contrasted with those recently established in the benzene series. Although the sum of the coupling constants for nitrothiophene falls on the line for the other substituents, the individual couplings deviate from the correlations, probably because of a strong mesomeric interaction.

THE existence of relationships between proton-proton coupling constants and substituent electronegativity has been demonstrated in several systems. The best known of these is the vinyl grouping,¹⁻³ exhibiting an approximately linear increase of all three couplings as electronegativity decreases. Other examples are mono-substituted ethanes,⁴⁻⁶ monosubstituted benzenes,^{7,8} *para*-disubstituted benzenes,⁸ and N-substituted pyridines.⁹

Although a wealth of data has been accumulated for substituted thiophenes,¹⁰ no attempt appears to have been made to establish a similar relationship for these compounds. The reasons for this are clear. Firstly, all the substituents in earlier studies have electronegativities in the comparatively small range of 2.5 to 3.5. Secondly, the variations in the couplings are very small, so that relatively small errors in measuring and analysing the spectra have caused these variations to appear unrelated to the nature of the substituent.

In this paper the range of electronegativities is extended and evidence presented of a well-defined correlation between the thiophene couplings and substituent electronegativity.

RESULTS

In Table 1 are reproduced the three coupling constants for the series of 2-substituted thiophenes, together with substituent electronegativities, E_x .

These values are plotted against electronegativity in Figs 1 and 2. The best lines through the points were determined by least squares analysis, and are defined as follows.

$$J_{35} = 0.44 E_x + 0.00$$

$$J_{34} = 0.33 E_x + 2.69$$

$$J_{45} = 0.58 E_x + 3.75$$

$$\Sigma J = 1.35 E_x + 6.45$$

TABLE 1

X	J_{35}	J_{34}	J_{45}	ΣJ	E_s^c
—Li ^a	0.5	2.8	4.3	7.6	0.95
—HgCl	0.65	3.41	4.98	9.04	1.9
—Pb(Thienyl) ₃	0.81	3.45	4.86	9.12	1.9
—Sn(Thienyl) ₃	0.78	3.33	4.84	8.95	1.9
—Si(Thienyl) ₃	0.87	3.44	4.65	8.96	1.9
—H ^b	1.06	3.44	5.15	9.65	2.3
—PCl ₂	1.12	3.66	4.90	9.69	—
—Me ^c	1.16	3.47	5.20	9.83	2.5
—I	1.24	3.62	5.48	10.34	2.7
—Br	1.36	3.65	5.59	10.60	3.0
—NH ₂	1.40	3.59	5.49	10.48	3.0
—Cl	1.49	3.69	5.62	10.80	3.2
—NO ₂	1.62	4.13	5.31	11.06	3.35
—OMe	1.48	3.80	5.82	11.10	3.5
—O ^t Bu	1.43	3.73	6.00	11.15	3.5
—F ^d	1.69	3.89	6.02	11.60	3.95

^a Ref 11, ^b Ref 12, ^c Ref 13, ^d Ref 14, ^e Ref 2.

TABLE 2

X	Shifts in c/s from TMS			Solvent and concentration
	ν_3	ν_4	ν_5	
—Pb(Thienyl) ₃	445.2	438.3	461.7	CDCl ₃ , 5%
—Sn(Thienyl) ₃	447.5	438.3	464.6	CDCl ₃ , 10%
—Si(Thienyl) ₃	444.3	428.9	458.0	CCl ₄ , 10%
—HgCl	425.0	437.4	460.0	Dioxan, 5%
—PCl ₂	443.8	412.8	453.2	Neat Liquid

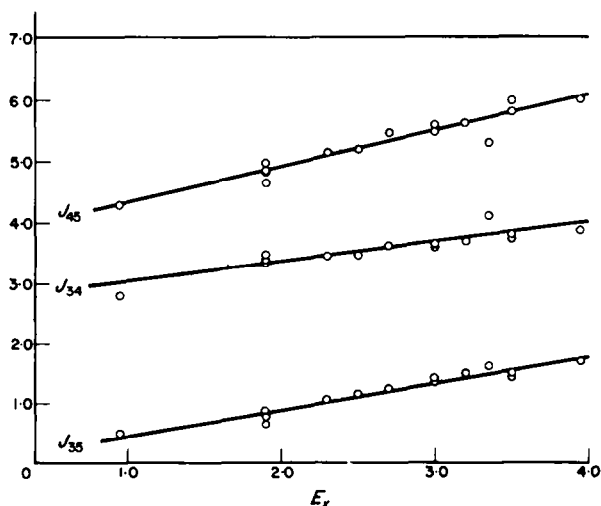
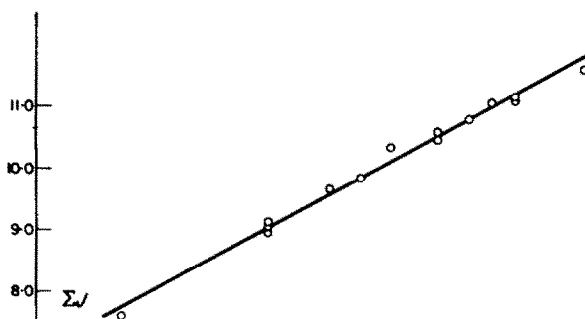


FIG. 1 Plots of J_{35} , J_{34} , and J_{45} vs. electronegativity E_s .

FIG. 2 Plot of sum of couplings vs. electronegativity, E_r .

The NMR spectra of several of these compounds have not previously been reported. Table 2 lists their respective chemical shifts.

In several instances, the ring protons were appreciably coupled to nuclei in the substituents. The first-order couplings are found in Table 3.

TABLE 3

$-X$	J_{x-H_3} (c/s)	J_{x-H_4}	J_{x-H_5}
$-\text{HgCl}$	118	32.4	71
$-\text{Pb}(\text{Thienyl})_3$	59	—	32
$-\text{PCl}_2$	6.5	1.9	0.0

In a few cases, C^{13} satellites were observed in the proton spectrum. The couplings measured from these spectra are listed in Table 4.

TABLE 4

X	$J(\text{C}_a^{13}-\text{H}_3)$	$J(\text{C}_a^{13}-\text{H}_4)$	$J(\text{C}_a^{13}-\text{H}_5)$
$-\text{I}$	173	169	188
$-\text{Cl}$	172	170	188
$-\text{NO}_2$	180	171	190
$-\text{OMe}$	167	168	189

Spectral analysis At 60 Mc/s many 2-substituted thiophenes present spectra which are nearly first-order. However, for the purposes of this work the couplings were required to an accuracy of better than 0.05 c/s. This was achieved by the use of a computer program based on the exact analysis of Castellano and Waugh.^{15, 3} In certain cases an alternative procedure was used, whereby the computer refined the first-order chemical shifts and couplings (read from the spectrum) until they converged upon the true parameters. In all cases the parameters obtained were put through the ABC calculation and reproduced the experimental spectra.

Since all three couplings are positive,¹⁶ no difficulty was encountered in assigning the transitions.

As an example, the observed and calculated spectra of 2-methoxythiophene are shown in Table 5.

TABLE 5. SPECTRUM OF 2-METHOXYTHIOPHENE FOR PARAMETERS:

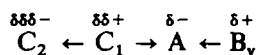
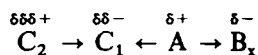
$$\begin{array}{lll} \nu_A = 394.11 & \nu_B = 380.95 & \nu_C = 363.29 \\ J_{AB} = 5.82 & J_{AC} = 3.80 & J_{BC} = 1.48 \end{array}$$

	Frequency (c/s from TMS)			Intensity (calculated)
	Observed	Calculated	Difference	
Comb	—	412.07	—	0.00
A	399.63	399.58	+0.05	0.55
A	395.94	395.94	0.00	0.63
A	393.71	393.75	-0.04	1.31
A	390.08	390.11	-0.03	1.60
B	384.07	384.10	-0.03	1.22
B	382.44	382.46	-0.02	1.59
B	378.31	378.27	+0.04	0.60
Comb	—	377.62	—	0.00
B	376.66	376.63	+0.03	0.59
C	365.75	365.77	-0.02	1.23
C	364.15	364.14	+0.01	1.01
C	362.15	362.14	+0.01	0.95
C	360.53	360.50	+0.03	0.81
Comb	—	348.66	—	0.00

DISCUSSION

From Figs 1 and 2 it is apparent that all three couplings increase with increasing electronegativity. The sum of the couplings gives a particularly good correlation, while the individual couplings exhibit rather more scatter. This may be partly due to the fact that the sum is obtainable directly from the spectrum, although the scatter in the individual couplings is larger than the acceptable error in their determination.

Castellano⁹ has discussed the corresponding trends for monosubstituted benzenes and N-substituted pyridines in terms of an inductive effect described by the following models:



where A = a carbon or nitrogen atom

B_x = electron-withdrawing substituent

B_y = electron-donating substituent

The transmission of charges alternates along the molecular framework, in contrast to the currently held theory that the polarization induced by B should decrease monotonically along the bonds.

These models were invoked to explain the observation that whereas vinyl couplings

all decrease with increase in electronegativity, the vicinal coupling between ortho and meta protons in monosubstituted benzenes increases with electronegativity.

It will be instructive in this work to compare the variations in the thiophene couplings with the corresponding variations in monosubstituted benzenes. To facilitate comparison the hydrogen atoms of the thiophene ring will be numbered to correspond with Castellano's numbering of the phenyl protons.⁹

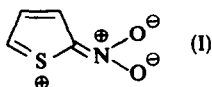


The variation of $J(1, 2)$ for both series is in accordance with the proposed model. However, $J(1, 3)$ for the thiophenes increases with electronegativity, this behaviour being in direct contrast to that required by the above model and exhibited by $J(1, 3)$ in the benzene series. Further, the coupling $J(2, 3)$ which remains virtually stationary for monosubstituted benzenes, exhibits the largest variation of all in the thiophenes.

It is clear that consideration of the carbon skeleton in terms of this inductive model cannot explain these observations. However, if an inductive effect operates through the easily polarizable sulphur sigma bonds, then an appreciable charge may be developed at position 3 by the substituent.

Other mechanisms proposed for substituent effects on vicinal couplings are (i) a shortening of the C—C bond length, the coupling being proportional to this length,^{17–20} and (ii) variations in C—C—H angles caused by changes in hybridization of the carbon bonded to the substituent.^{20–22} Neither of these is likely to operate in the thiophene $J(2, 3)$ coupling.

Castellano⁹ pointed out that his inductive mechanism is supported by the fact that the most effective substituents in altering $J(1, 2)$ are those for which it is hardest to write mesomeric structures. In this context it is interesting to note that nitrothiophene is the only compound departing significantly from the correlations in Fig. 1. The value of $J(1, 3)$ is acceptable, but $J(1, 2)$ is too large and $J(2, 3)$ much too small. If the mesomeric form I makes a significant contribution to the structure, the resulting alterations in the carbon-carbon bond lengths will affect the couplings in just this way.



The inductive effect of the substituent still operates through the sigma bonds, being superimposed upon the mesomeric effect. This would explain the very good agreement between the sum of the couplings and electronegativity. The values of J_{13c} for this compound also indicate the presence of some interaction not found in the other substituted thiophenes.*

The recently reported couplings for lithium thienyl,¹¹ and fluorothiophene¹⁴ came to my notice on completion of this work and have been included. Since these two substituents represent the extreme ends of the electronegativity scale, the close agreement between these data and the correlations in Figs. 1 and 2 is especially gratifying.

* Note added in Proof. The couplings for 2-cyanothiophene (1·19, 3·78, 5·03 c/s) show deviations similar to those for 2-nitrothiophene.

This work has not included any 3-substituted thiophenes, although the studies of Hoffman and Gronowitz¹⁰ reveal a relationship between the sum of the couplings and electronegativity similar to that in the 2-substituted compounds. The scatter in the values for the individual couplings is too great to allow any positive conclusions.

EXPERIMENTAL

The following compounds were synthesised for this study. References to their preparation are given in parenthesis.

2-Chloromercurithiophene	(23)	m.p. 183°
Lead tetra(2-thienyl)	(24)	m.p. 152–153°
Tin tetra(2-thienyl)	(24)	m.p. 155–156°
Silicon tetra(2-thienyl)	(25)	m.p. 134–135°
2-Thienyldichlorophosphine	(26)	b ₁₈ 108°
2-Iodothiophene	(27)	b ₁ 42–44°
2-Bromothiophene	(25)	b ₁₃ 43–46°
2-Aminothiophene	(10)	not isolated
2-Chlorothiophene	(28)	b ₇₆₀ 131–132°
2-Nitrothiophene	(29)	m.p. 44–45°
2-Methoxythiophene	(30)	b ₁₃ 52–53°
2-tert-Butoxythiophene	(31)	b ₁₃ 91–93°

NMR spectra were recorded on a Varian A 60 spectrometer. When a compound could not be studied as a neat liquid, it was dissolved in carbon tetrachloride or deuteriochloroform.

2-Nitrothiophene was studied in both deuteriochloroform and acetone.

2-Iodothiophene was studied as a neat liquid and also in nitromethane.

Neither compound showed any appreciable solvent dependence of the couplings.

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