

The Signs of the Side-chain Couplings in Methylthiophenes as Determined by Multiple Resonance Techniques

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The signs of the methyl couplings in 2-bromo-5-methylthiophene, 2-carboxymethyl-4-methylthiophene, and 4-methyl-3-thiophenealdehyde have been determined relative to those of the ring couplings by double and triple resonance techniques. The couplings between the methyl groups and their *ortho* hydrogens* were found to be of opposite sign to the ring coupling constants, while the methyl couplings to *meta* hydrogens carry the same sign as the ring coupling constants.

1. INTRODUCTION

The possibility of determining the signs of spin-spin coupling constants by multiple resonance techniques has led to an extensive study by several workers of the signs of couplings in different representative compounds. To obtain the signs and magnitudes of the coupling constants is of fundamental importance for attempts to theoretically account for these couplings. Confirmation of the current theories of the mechanisms of these coupling constants should also be obtained.

Of great interest in this connection is the study of the long-range side-chain couplings in substituted aromatic compounds, *e.g.* aldehyde and methyl compounds. The signs of the side-chain couplings in furfuraldehydes¹ and 2-thiophenealdehyde^{2,3} have been studied earlier by multiple resonance techniques. However, no satisfactory account for the mechanism of these long-range couplings has hitherto been given.

Karplus⁴ has theoretically investigated the contribution of π -electrons to the long-range couplings in non-conjugated unsaturated compounds. All experimental findings to date are in excellent agreement with his theory. The long-range methyl couplings in methyl substituted aromatic compounds have also been attributed to a π -electron transmitted contact mechanism.⁵⁻⁹ A corroboration of the correctness of this interpretation should be obtained by the determination of the signs of these couplings.

* In 2-carboxymethyl-4-methylthiophene the protons in 3- and 5-position are both *ortho* to the methyl group.

In this paper we report the determination of the signs of the methyl couplings in three different methylthiophenes as determined by double and triple resonance techniques.

2. METHOD

A simple and straightforward method for determining the relative signs of the spin coupling constants in a loosely coupled spin system is by selective decoupling.¹⁰⁻¹¹ A second r.f. field (H_2) is employed to perturb specific transitions in the spectrum, while related transitions are simultaneously recorded with the usual weak measuring r.f. field (H_1). For systems with all coupling constants small, this necessitates a careful calibration of the single resonance spectrum and monitoring of the decoupling frequency (ν_2). Applications of the selective decoupling method to molecules of type AKX_n have been described by Freeman and Whiffen and by Manatt and Elleman.¹¹⁻¹⁵

The compounds studied in this investigation, 2-bromo-5-methylthiophene, 2-carboxymethyl-4-methylthiophene, and 4-methyl-3-thiophenealdehyde, all show almost first order spectra, *i.e.* if we disregard the aldehyde coupling in 4-methyl-3-thiophenealdehyde.

The methyl couplings are in all cases smaller than the ring couplings. This makes the selective decoupling of the methyl couplings feasible for a determination of the signs of the methyl couplings relative to the ring coupling constants. The large shift between the methyl band and the ring hydrogen band also makes these experiments the simplest of those possible for a sign determination.

In 4-methyl-3-thiophenealdehyde, where the aldehyde proton couples into the ring (with hydrogen 5), the double resonance experiments are not as straightforward as in the simpler systems. However, by employing a triple resonance technique, in which a strong third r.f. field (H_3) is introduced to stir up the "supernumerary" nucleus (the aldehyde proton), the latter is effectively decoupled from the rest of the spectrum. The selective decoupling experiment can then be performed in the same way as in the simpler systems, as first discussed by Hoffman *et al.*¹

3. EXPERIMENTAL

The 4-methyl-3-thiophenealdehyde and 2-carboxymethyl-4-methylthiophene used in this investigation were synthesized by Professor Salo Gronowitz in connection with an investigation by Hoffman and Gronowitz of the coupling constants in disubstituted thiophenes.⁷ The samples used in that investigation could be utilized again, since no disturbing decomposition had occurred. TMS was added as internal reference for the calibration of the spectra. The 2-bromo-5-methylthiophene from the same investigation had decomposed and the sample used in this investigation was kindly synthesized by Fillic. Anna-Britta Hörnfeldt.

The spectra were obtained using a Varian Associates model V 4300 B spectrometer operating at a radiofrequency of 40.000 Mcps. The spectra were recorded by the use of phase sensitive detection by operating the Varian V 3521 integrator in the lower side-band mode. The single resonance spectra were calibrated using the side-band technique. The r.f. field H_2 was obtained through frequency modulation of the r.f. transmitter and the r.f. field H_3 by field modulation. For this two audio oscillators Philips model GM 2305

B were employed. The audio frequencies were monitored with a Hewlett-Packard model 524 D frequency counter. During the double resonance experiments it was found necessary to measure the oscillator frequency of the integrator at repeated intervals to keep pace with the long term drift.

4. RESULTS

4.1. 2-Bromo-5-methylthiophene. The single resonance spectrum of an 80 % cyclohexane solution of 2-bromo-5-methylthiophene is shown in Fig. 1. For

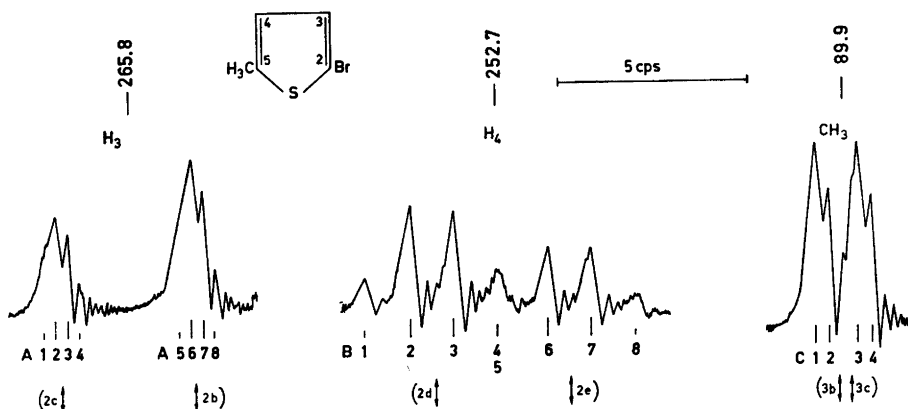


Fig. 1. NMR-spectrum at 40 Mcps of 2-bromo-5-methylthiophene in an 80 % cyclohexane solution. The shifts are given relative to TMS as internal reference. The methyl group band is shown with reduced gain. The arrows refer to the centerings of the decoupling r.f. fields in the experiments shown in Figs. 2 and 3.

convenience in the discussion of the double resonance experiments the transitions in this spectrum have been numbered. The methyl coupling constants are much smaller than the ring couplings and the 1:3:3:1 quartets obtained in the ring proton spectrum are separated, except for an overlap of two lines in the 4-hydrogen band. The experiment with selective decoupling of the methyl couplings by irradiation of these 1:3:3:1 quartets in the ring hydrogen bands can then conveniently be performed. This should lead to the collapse of specific lines in the methyl quartet.

The inverse experiment, *i.e.* irradiation in the methyl quartet while studying the ring proton spectrum, may also be performed. As discussed by Freeman *et al.*^{13,16} this latter experiment is the preferable one since the interpretation of the decoupled patterns is then less ambiguous. Irradiation of the A quartet in an AX₃ system with too low amplitude of H₂ while studying the X₃-doublet might lead to disturbing satellites near the collapsed line which may cause difficulties in the interpretation. These difficulties are not as easily encountered when the X₃ doublet is irradiated and the A quartet studied.

Due to the smallness of the methyl couplings in this case it is, however, evident that the difference in decoupling frequencies predicted for like and unlike signs of the methyl couplings relative to the ring coupling constant

Table 1. The results of the double resonance experiments on 2-bromo-5-methylthiophene

Spin couplings compared	Collapse of lines	Illustrated in figure	Notation	Predicted frequency differences		Observed frequency difference
				like signs	unlike signs	
J_{34} and J_{CH_3-4}	C_1 and C_2 C_3 and C_4	2 b	$\Delta\nu_{13}$	177.1	173.5	173.6
		2 c	$\Delta\nu_{24}$	174.7	178.3	178.5
			$\Delta\nu_{12} - \Delta\nu_{34}$	2.4	-4.8	-4.9
J_{34} and J_{CH_3-3}	C_1 and C_3 C_2 and C_4	2 d	$\Delta\nu_{13}$	164.4	160.8	164.2
		2 e	$\Delta\nu_{24}$	161.2	164.8	161.2
			$\Delta\nu_{13} - \Delta\nu_{24}$	3.2	-4.0	3.0
J_{34} and J_{CH_3-3}	B_1-B_4 B_5-B_8	3 b	$\Delta\nu_{14}$	-164.4	-164.8	-164.5
		3 c	$\Delta\nu_{68}$	-161.2	-160.8	-161.2
			$\Delta\nu_{14} - \Delta\nu_{68}$	-3.2	-4.0	-3.3

is much more pronounced in the experiment with irradiation in the ring proton spectrum. With sufficient amplitude of the decoupling H_2 field in the irradiation of the ring protons no difficulties due to partial collapse of the methyl group lines were encountered, and the interpretation of the results was clear. The criterion for optimum decoupling frequency was the maximum peak height of the collapsed line. The uncertainty in this frequency is estimated to 0.3 cps.

The results of the spin decoupling experiments are given in Table 1. The predicted frequency differences $\nu_2 - \nu_1$ for the different relative sign possibilities calculated from the known magnitudes of shifts and couplings are included as well as the lines collapsed. It may not be necessary to do all the decoupling experiments presented for a determination of the relative signs. For example, in the case of comparison between the signs of J_{34} and J_{CH_3-4} it is in principle only necessary to set the modulation $\nu_2 - \nu_1$ frequency to irradiate the quartet $A_5 - A_8$ and observe the $C_1 - C_2$ doublet collapse with a careful measurement of the optimum decoupling frequency. However, a more unambiguous determination may be made by stepwise changing the modulating frequency until the $C_3 - C_4$ doublet collapses. A favourable comparison of the separation of these two decoupling frequencies with the predicted ones is then a better criterion for the correctness of the sign determination, as discussed by Hoffman *et al.*¹ These differences between different decoupling frequencies are included in the table.

In Figs. 2 and 3 the results of the double irradiation experiments given in Table 1 are displayed. Fig. 2 shows the effects on the methyl band for irradiating the four 1:3:3:1 quartets in the ring proton spectrum. The agreement between predicted and observed irradiating frequencies is very good and no ambiguity exists in the interpretation of the results.

In the determination of the sign of J_{CH_3-3} relative to that of J_{34} the reverse experiment with irradiation in the methyl group while studying the 4-hydrogen multiplet was also performed. The result is shown in Fig. 3. This experiment

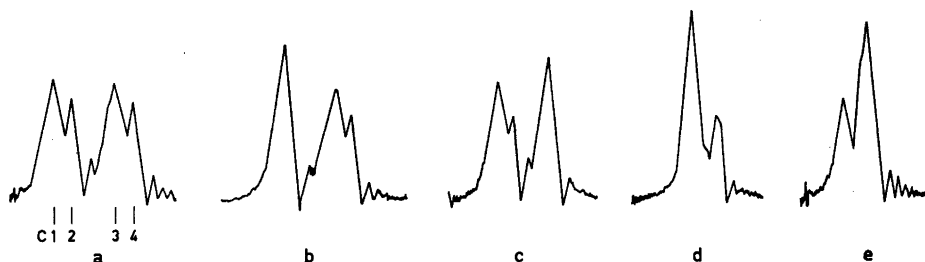


Fig. 2. The methyl group region of Fig. 1. (a) shows the single resonance spectrum and (b-e) the spectrum in the presence of a decoupling r.f. field centered at the position shown by the corresponding arrow in Fig. 1.



Fig. 3. The region of the 4-proton of Fig. 1. (a) shows the single resonance spectrum and (b-c) the spectrum in the presence of a decoupling r.f. field, centered at the position shown by the corresponding arrow in Fig. 1.

is rather tricky since the difference between the frequencies of optimum decoupling predicted for like and unlike signs is only 0.4 cps. As the uncertainty in the determination of the optimum decoupling frequency is 0.3 cps, unambiguous conclusions cannot be drawn from these frequencies alone. Somewhat more confidence in the result of this experiment is, however, achieved by comparison of the separation of the observed optimum decoupling frequencies for the two multiplets concerned with those predicted for like and unlike signs. The result, that J_{34} and J_{CH_2-3} are of like signs, is also consistent with that of the reverse experiment, which is quite unambiguous.

As a result we thus find that the J_{CH_2-3} coupling constant has the same sign as the ring coupling constant while J_{CH_2-4} is of opposite sign. This is consistent with earlier findings by Hoffman and Gronowitz,¹⁷ that the two methyl couplings are of unequal signs. However, by the ABX_3 analysis then performed these signs could not be determined relative to that of the ring coupling constant.

4.2 2-Carboxymethyl-4-methylthiophene. The single resonance spectrum of a 39 % cyclohexane solution of 2-carboxymethyl-4-methylthiophene is shown in Fig. 4. Traces of impurities were seen in the ring proton part, which, however

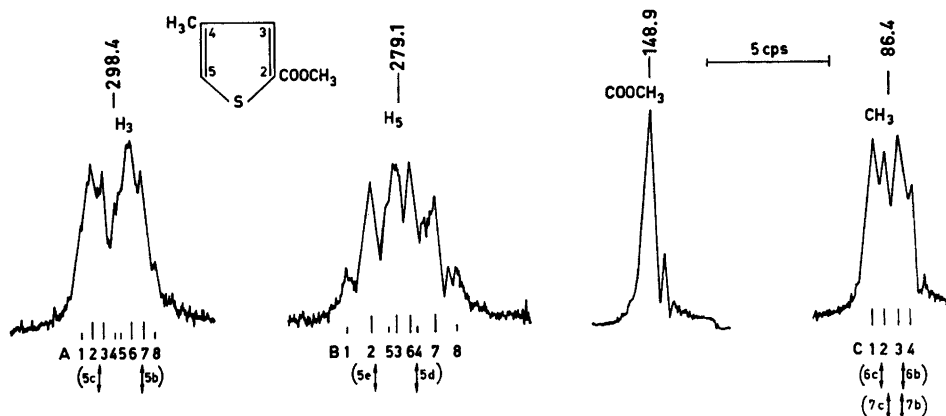


Fig. 4. NMR-spectrum at 40 Mcps of 2-carboxymethyl-4-methylthiophene in a 39 % cyclohexane solution. The shifts are given relative to TMS as internal reference. The methyl group bands are shown with reduced gain. The arrows show the centerings of the decoupling r.f. fields in the experiments shown in Figs. 5-7.

cause no trouble in the double resonance experiments. The carboxymethyl group does not couple to any other proton in the system and can consequently be disregarded. Due to the smallness of the ring proton coupling constant (1.6 cps) a partial overlap of the two 1:3:3:1 quartets with a splitting of 1.05 cps in the 5-hydrogen band is obtained. However, by a careful choice of the amplitude of the H_2 r.f. field it is still possible to perform a selective decou-

Table 2. The results of the double resonance experiments on 2-carboxymethyl-4-methylthiophene.

Spin couplings compared	Collapse of lines	Illustrated in figure	Notation	Predicted frequency differences		Observed frequency difference
				like signs	unlike signs	
J_{35} and J_{CH_3-5}	C_1 and C_2	5 b	$\Delta\nu_{12}$	212.2	210.7	210.6
		5 c	$\Delta\nu_{34}$	211.7	213.2	213.2
				$\Delta\nu_{12} - \Delta\nu_{34}$	0.5	-2.5
J_{35} and J_{CH_3-5}	$A_1 - A_4$	6 b	$\Delta\nu_{14}$	-212.2	-213.2	-213.1
		6 c	$\Delta\nu_{58}$	-211.7	-210.7	-210.8
				$\Delta\nu_{14} - \Delta\nu_{58}$	-0.5	-2.5
J_{35} and J_{CH_3-3}	C_1 and C_3	5 d	$\Delta\nu_{13}$	193.3	191.7	192.1
		5 e	$\Delta\nu_{24}$	192.1	193.7	194.1
				$\Delta\nu_{13} - \Delta\nu_{24}$	1.2	-2.0
J_{35} and J_{CH_3-3}	$B_1 - B_4$	7 b	$\Delta\nu_{14}$	-193.3	-193.7	-193.8
		7 c	$\Delta\nu_{58}$	-192.1	-191.7	-191.9
				$\Delta\nu_{14} - \Delta\nu_{58}$	-1.2	-2.0

pling experiment with irradiation of these quartets leading to a clear collapse of specific lines in the methyl band.

The decoupling experiments performed were analogous to those in the previous case. The results are summarized in Table 2. Fig. 5 shows the methyl

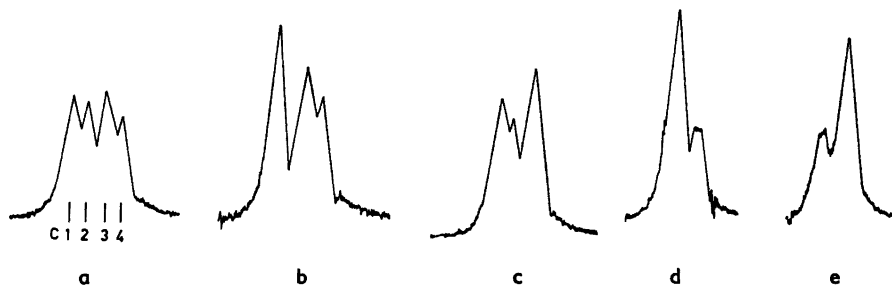


Fig. 5. The methyl group region of Fig. 4. (a) shows the single resonance spectrum and (b–e) the spectrum in the presence of a decoupling r.f. field, the centering of which is indicated by the corresponding arrow in Fig. 4.

group, unperturbed (a) and during irradiation of the ring protons (b–e). From experiments (b) and (c) it is evident that the J_{CH_3-5} coupling is of opposite sign to the ring coupling constant. The reverse experiments to (b) and (c), *i.e.* irradiation of the methyl group and observation of the 3-hydrogen multiplet was also performed and the obtained patterns are shown in Fig. 6. The

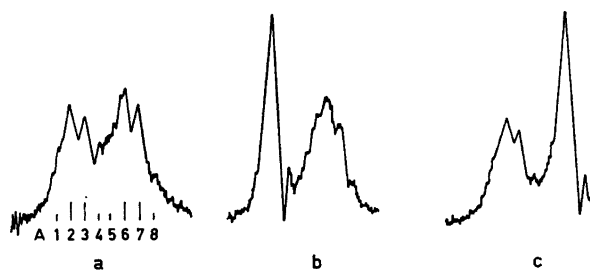


Fig. 6. The region of the 3-proton of Fig. 4. (a) shows the single resonance spectrum and (b–c) the spectrum in the presence of a decoupling r.f. field, the centering of which is indicated by the corresponding arrow in Fig. 4.

sign obtained for J_{CH_3-5} is thus further confirmed, and the agreement between predicted and measured decoupling frequencies is very good in both experiments.

In the decoupling of the J_{CH_3-5} coupling (Fig. 5, d,e) the frequencies for optimum decoupling were not as easily determined, due to the partial overlap of the 1:3:3:1 quartets in the 5-hydrogen band. The decoupling frequencies show good agreement with those predicted for unlike signs of J_{35} and J_{CH_3-3} , an interpretation which is also the only one consistent with the measured separation of these frequencies.

The result of the reverse experiment, *i.e.* irradiation of the methyl group while studying the 5-hydrogen band, is shown in Fig. 7. The separation between

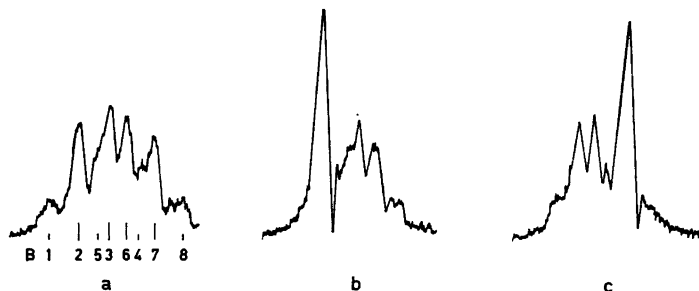


Fig. 7. The region of the 5-proton of Fig. 4. (a) shows the single resonance spectrum and (b–c) the spectrum in the presence of a decoupling r.f. field, the centering of which is indicated by the corresponding arrow in Fig. 4.

the decoupling frequencies predicted for like and unlike signs of J_{35} and J_{CH_3-3} is only 0.4 cps. As this is of the same magnitude as the uncertainty in the measured optimum decoupling frequencies, the interpretation of this experiment is not altogether unambiguous. The difference between the two decoupling frequencies, however, shows agreement with that predicted for unlike signs only, which is also consistent with the result of the reverse experiment.

We thus conclude that both side-chain couplings J_{CH_3-3} and J_{CH_3-5} are of opposite sign to the ring coupling constant J_{35} .

4.3. *4-Methyl-3-thiophenealdehyde*. The single resonance spectrum of pure liquid 4-methyl-3-thiophenealdehyde is shown in Fig. 8.

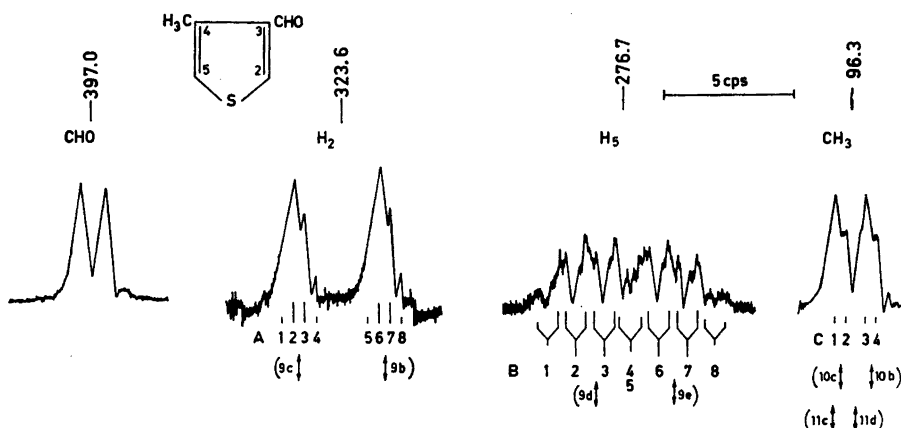


Fig. 8. NMR-spectrum at 40 Mcps of pure liquid 4-methyl-3-thiophenealdehyde. The shifts are given relative to TMS as internal reference. The side-chain bands are shown with reduced gain. The arrows refer to the corresponding Figs. 9–11 and show the centerings of the decoupling r.f. fields in the double resonance experiments.

This spectrum is somewhat more complicated than the previous ones, as the aldehyde proton couples into the ring system. The 5-hydrogen band becomes a complicated multiplet with overlapping of lines which makes a selective decoupling experiment analogous to the previous ones difficult. However, by introducing a third strong r.f. field centered upon the aldehyde doublet the aldehyde proton is effectively decoupled from the remaining system, in which the sign determining decoupling experiments can be performed as in the previous cases.

The results of the selective decoupling experiments are given in Table 3. The determination of the relative signs of the J_{25} and J_{CH_3-5} couplings were made both by irradiation in the 2-hydrogen band while studying the methyl quartet as well as the reverse experiment. Decoupling of the aldehyde proton is irrelevant in these experiments. The patterns obtained are shown in Fig. 9, (b, c) and Fig. 10, (b, c). The agreement between the optimum decoupling

Table 3. The results of the triple resonance experiments on 4-methyl-3-thiophenealdehyde.

Spin couplings compared	Collapse of lines	Illustrated in figure	Notation	Predicted frequency differences		Observed frequency difference
				like signs	unlike signs	
J_{25} and J_{CH_3-5}	C ₁ and C ₂ C ₃ and C ₄	9 b	$\Delta\nu_{13}$	228.4	225.2	225.3
		9 c	$\Delta\nu_{34}$	226.3	229.5	229.6
			$\Delta\nu_{13} - \Delta\nu_{34}$	2.1	-4.3	-4.3
J_{25} and J_{CH_3-5}	A ₁ -A ₄ A ₅ -A ₈	10 b	$\Delta\nu_{14}$	-228.4	-229.5	-229.5
		10 c	$\Delta\nu_{58}$	-226.3	-225.2	-225.3
			$\Delta\nu_{14} - \Delta\nu_{58}$	-2.1	-4.3	-4.2
J_{25} and J_{CH_3-2}	C ₁ and C ₃ C ₂ and C ₄	9 d	$\Delta\nu_{13}$	181.9	178.7	181.6
		9 e	$\Delta\nu_{24}$	179.0	182.2	178.9
			$\Delta\nu_{13} - \Delta\nu_{24}$	2.9	-3.5	2.7
J_{25} and J_{CH_3-2}	B ₁ -B ₄ B ₅ -B ₈	11 c	$\Delta\nu_{14}$	-181.9	-182.2	-181.2
		11 d	$\Delta\nu_{58}$	-179.0	-178.7	-178.6
			$\Delta\nu_{14} - \Delta\nu_{58}$	-2.9	-3.5	-2.6

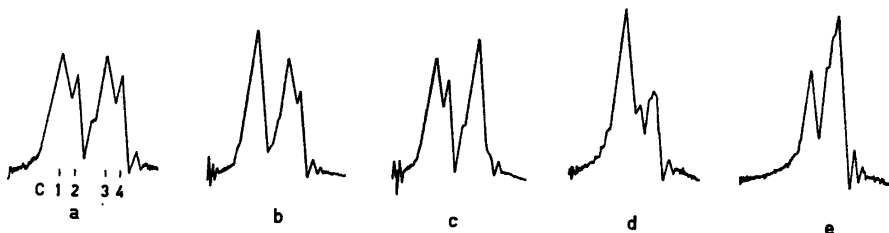


Fig. 9. The methyl group region of Fig. 8. (a) shows the single resonance spectrum and (b-e) the spectrum in the presence of a decoupling r.f. field centered as indicated by the corresponding arrow in Fig. 8. In (d-e) an additional strong r.f. field was centered at the aldehyde band (mod. freq. 119 cps) to decouple the $J_{\text{CHO}-5}$ coupling.

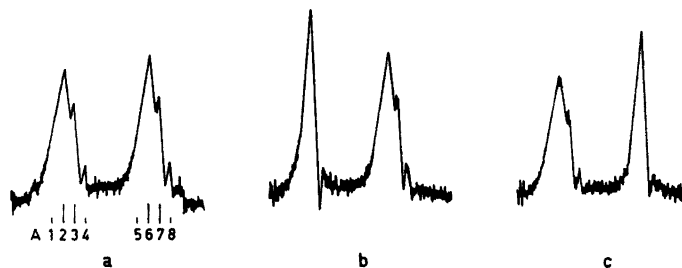


Fig. 10. The region of the 2-proton of Fig. 8. (a) shows the single resonance spectrum and (b–c) the spectrum in the presence of a decoupling r.f. field, centered as indicated by the corresponding arrow in Fig. 8.

frequencies and the predicted ones for unlike signs of the couplings is very good.

In determining the relative signs of J_{CH_3-2} and J_{25} the aldehyde group was irradiated by a strong r.f. field (modulating frequency 301 cps) in addition to the decoupling by irradiation in the 5-hydrogen band. The methyl patterns obtained are shown in Fig. 9, (d, e). The decoupling frequencies are only consistent with an assignment of like signs of these couplings.

In the reverse experiment the aldehyde proton was decoupled by a strong r.f. field (modulating frequency 119 cps) in addition to the decoupling by irradiation in the methyl band. The 5-hydrogen patterns obtained are shown in Fig. 11, (b-d). The agreement between the measured optimum decoupling

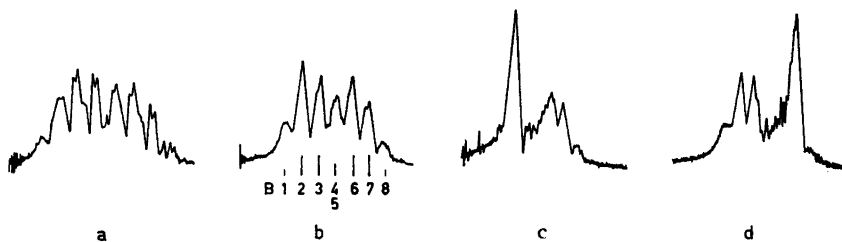


Fig. 11. The band of the 5-proton of Fig. 8. (a) shows the single resonance spectrum and (b) the spectrum in the presence of a strong r.f. field, centered at the aldehyde band (mod. freq. 301 cps) to decouple the $J_{\text{CHO}-5}$ coupling. In (c–d) the decoupling r.f. field, indicated by the corresponding arrow in Fig. 8. has been added.

frequencies and the predicted ones is not good, and unambiguous conclusions cannot be drawn from this experiment alone. This discrepancy between the predicted and experimental frequencies might partly be due to second order shifts of the hydrogen bands due to the presence of the strong r.f. field H_3 .¹⁸

As a result we find that J_{25} and J_{CH_3-5} have unequal signs while J_{CH_3-2} carries the same sign as the ring coupling constant J_{25} .

5. CONCLUSION

The ring coupling constants in thiophene all carry the same sign. This has been determined by the careful analysis of the high-resolution spectra of substituted thiophenes^{18,19} and also confirmed directly by double irradiation experiments.²⁰ From the experiments discussed in this paper it can then be concluded that in methylthiophenes, the couplings between the methyl group and its *ortho* hydrogens are of opposite sign to the ring coupling constants while the couplings between the methyl group and its *meta* hydrogens carry the same sign as the ring couplings.

Theoretically it is predicted that the couplings between protons attached to vicinal carbons are positive in sign.²¹ This has been directly confirmed experimentally for benzenes, where the *ortho* coupling constant has been determined to be positive.²² From this absolute sign it is possible by analogies and by relative sign determinations to obtain the absolute sign of a wide range of couplings.

The ring coupling constants in thiophene can thus safely be assumed to be absolutely positive in sign. One can then also conclude that the couplings between the methyl group and its *ortho* hydrogens in the methylthiophenes are negative in sign while the couplings between the methyl group and its *meta* hydrogens are positive in sign. This can probably be extrapolated to other methylsubstituted aromatic hydrocarbons.

These long-range methyl couplings have been attributed to a π -electron transmitted contact coupling mechanism, an interpretation which has been supported by indirect evidence.^{5-9,23}

The long-range couplings between protons in aromatic (and also acyclic unsaturated) compounds are partly ascribed to a π -electron transmitted mechanism. In benzene this contribution is estimated to be small ($\lesssim 1$ cps)²⁴ and is concealed by the stronger σ -electron transmitted couplings in the *ortho* and *meta* couplings. It should dominate the *para* coupling, however as the σ -couplings in contrast to the π -electron couplings are rapidly attenuated as the number of intervening bonds increases.

If a directly bound proton is substituted by a methyl group it is predicted that the π -electron transmitted coupling should remain almost unchanged in magnitude, but obtain the reverse sign.^{4,8} This theoretical prediction has been confirmed for acyclic unsaturated compounds, where such methyl substitutions have been performed (for a review see Ref.²³).

The substitution of a proton directly bond to the sp^2 or sp hybridized carbons by a methyl group then gives the possibility of estimating the π -electron contribution to the couplings in unsaturated compounds. By a determination of the signs of the methyl couplings one can consequently also derive the absolute sign of these π -electron transmitted couplings.

The π -electron contribution to the proton spin couplings in benzene and naphthalene have been calculated by McConnell.²⁵ It is predicted that for even alternate hydrocarbons the π -electron transmitted spin coupling should be positive for protons separated by an odd number of bonds and negative for protons separated by an even number of bonds.^{25,26}

No corresponding calculations have been undertaken for thiophene so far. However, it can probably be assumed that this result holds also for the J_{23} , J_{24} and J_{34} couplings in thiophene, although strictly it is not an even alternate hydrocarbon,

This is in complete agreement with the signs of the π -electron contributions to the spin couplings obtained from the present study of the methyl couplings, as seen from the above discussion.

Acknowledgements. The authors wish to express their sincere thanks to Professor Kai Siegbahn for his interest in this work and all facilities out at their disposal. We are indebted to Fillic. A.-B. Hörnfeldt for synthesizing the 2-bromo-5-methylthiophene used in this investigation and to Professor Salo Gronowitz for placing the 4-methyl-3-thiophenealdehyde and 3-carboxymethylthiophene samples at our disposal. We also wish to thank Dr. Ragnar A. Hoffman for many helpful discussions during the completion of this work.

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Received June 25, 1964.