The Signs of the Methyl-Methyl Spin Couplings in 2,3-Dimethylthiophene, 2,3-Dimethylfuran, and 3-Iodo-2,5-dimethylfuran

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The signs and magnitudes of the methyl-methyl couplings in 2,3-dimethylthiophene, 2,3-dimethylfuran and 3-iodo-2,5-dimethylfuran have been determined by the selective decoupling technique. They were all found to be of the same sign as that of the ring couplings.

The signs and magnitudes are discussed in terms of σ- and π-electron contributions to the spin couplings.

1. INTRODUCTION

The signs of the methylcouplings in methylthiophenes and methylfurans have been determined in three preceding papers [1-3] and have been discussed in terms of π-electron and σ-electron contributions. It was found that the coupling $J_{(CH_3)2-(CH_3)5}$ in 3-acetyl-2,5-dimethylthiophene is 0.55 cps, whereas the coupling J_{CH_3-5} in 3-nitro-2-methylthiophene is only 0.15 cps. Since the former coupling can safely be assumed to be π-electron transmitted,[2,4,5] these results support the suggestion that there is a partial cancellation of a negative π-electron contribution and a positive σ-electron contribution to the coupling J_{CH_3-5} in 2-methylthiophenes.[2] The coupling J_{CH_3-5} in 2-methylfuran is found to be -0.40 cps,[3] which is considerably larger than the J_{CH_3-5} coupling in thiophenes. In order to account for this coupling in terms of σ- and π-electron contributions we have, in fulfillment of an earlier suggestion,[3] studied 3-iodo

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2,5-dimethylfuran. To complete the study of methyl-methyl couplings in thiophenes and furans we have also studied 2,3-dimethylthiophene and 2,3-dimethylfuran.

In the present sign determinations the selective double irradiation method has been used, which is straightforward when applied to first order spectra and has been thoroughly discussed in preceding papers.[6-8] In the study of the compounds in this paper it has, however, not been quite trivial to perform and interpret the experiments due to the small couplings and the large number of lines and the fact that two of the compounds do not give first order spectra. Therefore we have thought it advisable to describe the sign investigations below in more detail than at first sight might seem necessary.

2. EXPERIMENTAL

The 2,3-dimethylthiophene was the same as in an earlier investigation of disubstituted thiophenes.[9]

3-Iodo-2,5-dimethylfuran, b.p. 64.5—65°/10 mm, was prepared through iodination of 2,5-dimethyl-3-furylmercuric chloride, obtained through mercuration of 2,5-dimethylfuran with mercuric chloride, with iodine in potassium iodide solution.[10]

2,3-Dimethylfuran, b.p. 92°/750 mm, was prepared in the following way. Methyl 2-furoate, b.p. 180—181°/760 mm, was chloromethylated with paraformaldehyde, zinc chloride and dichloroethane to methyl 5-(chloromethyl)-2-furoate, b.p. 136—138°/8 mm, which after treatment with zinc and acetic acid gave methyl 5-methyl-2-furoate, b.p. 92—94°/10 mm that was chloromethylated to methyl 4-(chloromethyl)-5 methyl-2-furoate, b.p. 108—109°/1 mm, which by treatment with zinc and acetic acid yielded methyl 4,5-dimethyl-2-furoate, b.p. 78—81°/1 mm, which was hydrolyzed to 4,5-dimethyl-2-furoic acid, m.p. 153—155°, which finally upon heat decarboxylation yielded 2,3-dimethylfuran.[11]

The spectra at 40 Mcps 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 sideband technique.

The single resonance spectra shown at 60 Mcps were obtained on a Varian model A 60 spectrometer. The recordings at 60 Mcps were made in order to make an interpretation of the single resonance spectra easier.

In the double resonance spectra the rf. field H_2 with frequency ν_2 was obtained by frequency modulation of the rf. transmitter. The frequency of the measuring field is denoted ν_1. The modulation frequency was produced by a Philips oscillator PP 6050. The audio frequencies were measured with Hewlett-Packard frequency counters models 524 D and 3734 A.

3. RESULTS

3.1. 2,3 - D i m e t h y l t h i o p h e n e

The single resonance spectrum at 40 and 60 Mcps of pure liquid 2,3-dimethylthiophene is shown in Fig. 1 and appears as an ABR_3X_3 spectrum. The compound has been studied earlier.[9] The fine structure caused by the couplings between the side-chain protons and the ring protons could not be resolved at that time. By making use of the known magnitudes of the methyl couplings in thiophenes one may assign the low field part of the AB spectrum to the ring proton in the 5 position [2,6,9] and the high field part to the ring
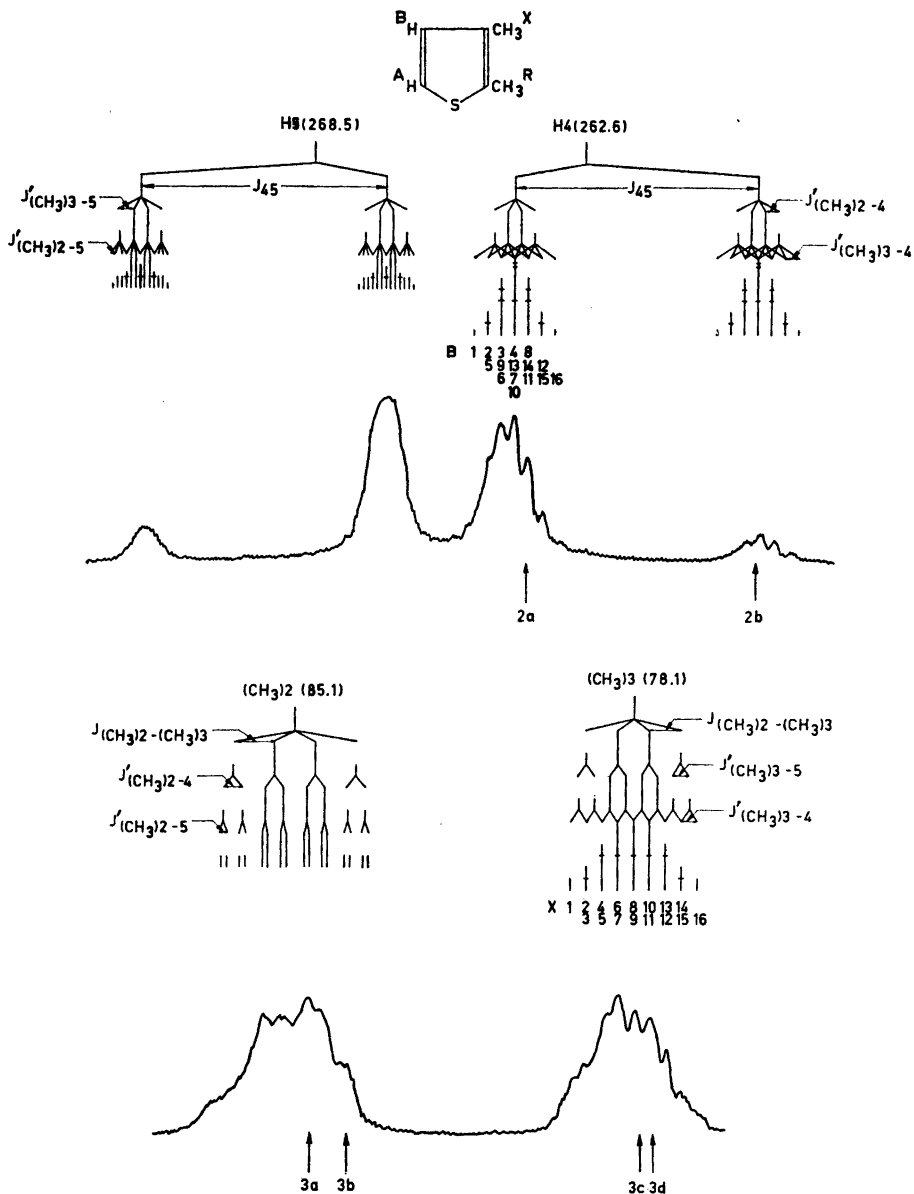
Fig. 1a. PMR spectrum at 40 Mcps of pure liquid 2,3-dimethylthiophene. The methyl bands and the ring proton band have been recorded with different gain. The shifts are given relative to TMS as internal reference. The methylcouplings with the ring protons are primed to indicate that they denote splittings and not exactly couplings. Some of the lines are numbered for future reference and the arrows refer to the double irradiation experiments shown in Figs. 2 and 3.
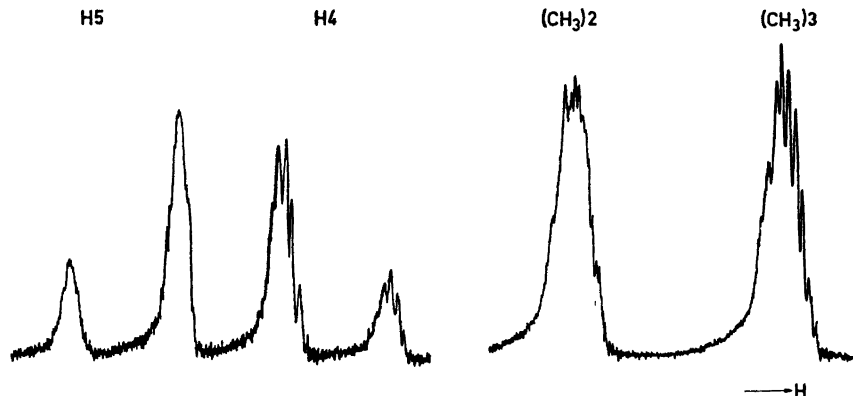
H5   H4   (CH$_3$)2   (CH$_3$)3

——→H

Fig. 1b. PMR spectrum at 60 Mcps of the same sample as in Fig. 1a.

proton in the 4 position. Analogously the low field methyl band is assigned to the 2-methyl group.

As seen from the spectrum the methyl-couplings with the 4-hydrogen are of equal magnitude and the couplings of the ring protons with the 3-methyl group are equal and half the size of the methyl-methyl coupling. The coupling $J_{(CH_3)2\text{-}5}$ is too small ($\leqslant 0.2$ cps) [2,9] to give observable splittings but large enough to broaden the 5-hydrogen and the 2-methyl spectrum.

Since the methyl-methyl coupling $J_{(CH_3)2\text{-}(CH_3)3}$ is only one tenth (even at 40 Mcps) of the corresponding shift difference we can apply first order analysis and the coupling can be obtained from the corresponding splittings. The numerical values of the methyl-ring proton couplings are not equal to the corresponding splittings, as the ring protons are rather strongly coupled. Approximate corrections obtained from the expressions for the splittings in the ABX_3Y_3 case can be applied to convert the splittings into the coupling constants.[*,9]

The couplings obtained are (in cps):

$$|J_{45}| = 5.30 \qquad |J_{(CH_3)2\text{-}(CH_3)3}| = 0.70 \qquad |J_{(CH_3)2\text{--}5}| \leqslant 0.2$$

$$|J_{(CH_3)2\text{--}4}| = |J_{(CH_3)3\text{--}4}| = |J_{(CH_3)3\text{--}5}| = 0.40$$

The value of the methyl-methyl coupling agrees well with that found earlier in 4,5-disubstituted 2,3-dimethyl thiophenes.[12]

Because of the strong coupling between A and B the splittings collapsed in the present double irradiation experiments do not correspond to couplings in the first order sense, but the nomenclature will be retained for simplicity.

In order to confirm the above assignment a double resonance experiment was performed. We studied the assigned 3-methyl group while we were irradiating in the ring proton spectrum. The amplitude was made large enough to

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* The corrections have been calculated at 60 Mcps.

Table 1. The results of the strong irradiation of the ring-proton band while studying the 3-methyl spectrum in 2,3-dimethylthiophene.

Collapse of lines	Notation	Predicted frequency differences (in cps) $J_{45}\cdot J_{(CH_3)3-5}>0$	$J_{45}\cdot J_{(CH_3)3-5}<0$	Observed frequency differences (in cps) $J_{45}\cdot J_{(CH_3)3-5}<0$	Illustrated in figure
X1, X2; X5, X6; X9, X10; X13, X14;	$\Delta\nu_1$	186.0	180.7	185.7	2a
X3, X4; X7, X8; X11, X12; X15, X16;	$\Delta\nu_2$	181.0	186.3	181.1	2b
	$\Delta\nu_1-\Delta\nu_2$	5.0	-5.6	4.6	

Collapse of lines	Notation	$J_{45}\cdot J_{(CH_3)3-4}>0$	$J_{45}\cdot J_{(CH_3)3-4}<0$	$J_{45}\cdot J_{(CH_3)3-4}<0$	
X1, X3; X5, X7; X9, X11; X13, X15;	$\Delta\nu_3$	193.9	188.6	188.6	
X2, X4; X6, X8; X10, X12; X14, X16;	$\Delta\nu_4$	188.9	194.2	194.3	
	$\Delta\nu_3-\Delta\nu_4$	5.0	-5.6	-5.7	

Table 2. The results of the decoupling of $J_{(CH_3)2-4}$ and $J_{(CH_3)3-4}$, respectively, in 2,3-dimethylthiophene.

Collapse of lines	Notation	Predicted frequency differences (in cps)[a] $J_{(CH_3)2-(CH_3)3}\cdot J_{(CH_3)3-4}>0$	$J_{(CH_3)2-(CH_3)3}\cdot J_{(CH_3)3-4}<0$	Observed frequency differences (in cps) $J_{(CH_3)2-(CH_3)3}\cdot J_{(CH_3)3-4}<0$	Illustrated in figure
B2, B6, B10, B14	$\Delta\nu_{2-14}$	-179.0	-179.7	-180.2	3b
B3, B7, B11, B15	$\Delta\nu_{3-15}$	-179.4	-178.7	-179.3	3a
	$\Delta\nu_{2-14}-\Delta\nu_{3-15}$	0.4	-1.0	-0.9	

Collapse of lines	Notation	$J_{(CH_3)2-(CH_3)3}\cdot J_{(CH_3)2-4}>0$	$J_{(CH_3)2-(CH_3)3}\cdot J_{(CH_3)2-4}<0$	$J_{(CH_3)2-(CH_3)3}\cdot J_{(CH_3)2-4}<0$	
B5—B8	$\Delta\nu_{5-8}$	-185.8	-186.5	-186.3	3c
B9—12	$\Delta\nu_{9-12}$	-186.2	-185.5	-186.6	3d
	$\Delta\nu_{5-8}-\Delta\nu_{9-12}$	0.4	-1.0	0.3	

[a] The known signs and magnitudes of the couplings $J_{(CH_3)2-5}$ and $J_{(CH_3)3-5}$ have been used in the calculation of the predicted frequency differences.
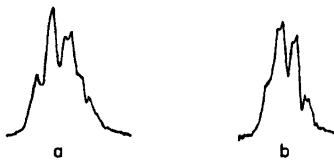
Fig. 2. Spectrum of the 3-methyl protons in the presence of a strong rf. field H_2 centered at the positions shown by the corresponding arrows in Fig. 1a.

decouple the 3-methyl couplings independent of the spin state of the other methyl group. The signs obtained for $J_{(CH_3)3-4}$ and $J_{(CH_3)3-5}$ are in agreement with known signs of these couplings,[1,2] *cf.* Table 1. If the assignment had been wrong this should not have been the case. Some of the collapsed line patterns corresponding to the entries in Table 1 are shown in Fig. 2.

To get the sign of the methyl-methyl coupling we made a selective irradiation in the methyl bands while recording the low-field part of the 4-hydrogen band. The results of these experiments are collected in Table 2 and the collapsed spectra are shown in Fig. 3. The experiments were in both cases restricted to the transitions belonging to $\pm \frac{1}{2}$ spin states of the nonirradiated methyl group. In the interpretation we use the known signs of the ring proton-

Fig. 3. Results of the selective double irradiation experiments in 2,3-dimethylthiophene; (a, b) and (c, d) show the low field part of the 4-hydrogen band for selective decoupling of $J_{(CH_3)2-4}$ and $J_{(CH_3)3-4}$, respectively. The corresponding positions of the decoupling rf. field are indicated by arrows in Fig. 1a.

methyl couplings relative to that of the ring couplings. To calculate the predicted frequency differences we have used the fact that the sign of $J_{(CH_3)2-5}$ is opposite to that of the couplings J_{45} and $J_{(CH_3)3-5}$.[1,2]

Table 2 shows that the observed optimum decoupling frequencies and their differences are only consistent with the assumption that $J_{(CH_3)2-(CH_3)3}$ carries the same sign as $J_{(CH_3)2-4}$ and the opposite sign to that of $J_{(CH_3)3-4}$. The experimentally determined decoupling frequencies for this sign alternative do not exactly agree with the predicted ones. A comparison of the differences between the latter frequencies and the differences between the former ones, is, however, a better criterion for a sign determination [6,13] and gives unambiguously the sign of $J_{(CH_3)2-(CH_3)3}$. As the signs of $J_{(CH_3)2-4}$ and of $J_{(CH_3)3-4}$ are known relative to that of the ring couplings we can conclude that $J_{(CH_3)2-(CH_3)3}$ carries the same sign as the ring couplings.

3.2. 2,3-Dimethylfuran

The single resonance spectrum of a 20 % solution of 2,3-dimethylfuran in carbon tetrachloride at 40 and 60 Mcps is shown in Fig. 4, where the lines are numbered for future reference. It is a first order AMR_3X_3 spectrum. Both spectra of the ring protons show the pattern of two partly overlapping septets, which means that for each ring proton the two methyl couplings are of the same size. The methyl bands consist of nine lines (fitting the intensity ratio 1:2:4:6:6:6:4:2:1) which indicates that for each methyl group the couplings to the ring protons are equal and half the size of the coupling between the methyl groups. Thus all the methyl to ring proton couplings are equal. All
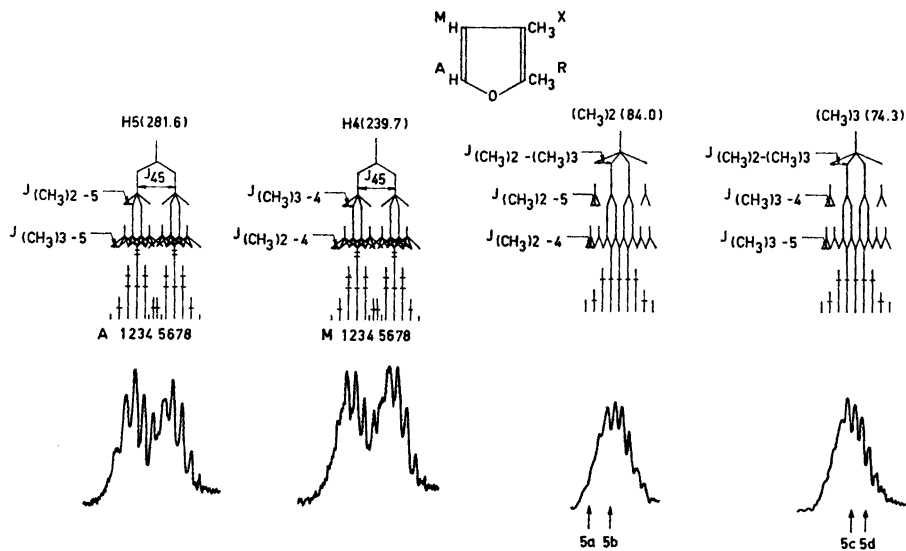

Fig. 4a. PMR spectrum at 40 Mcps of 2,3-dimethylfuran in a 20 % carbontetrachloride solution. The methyl bands have been recorded with reduced gain. The shifts are given relative to TMS as internal reference. The arrows refer to the double resonance experiments shown in Fig. 5.
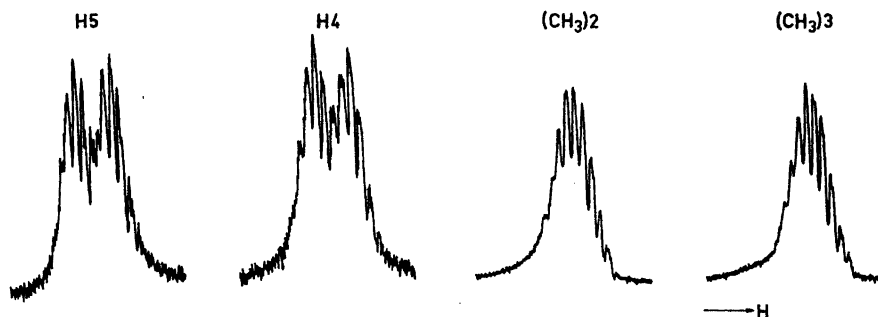

Fig. 4b. PMR spectrum at 60 Mcps of the same sample as in Fig. 4a.

the couplings except $J_{(CH_3)2-(CH_3)3}$ which has not previously been determined, agree with earlier results.[3,14,15]

The couplings obtained are (in cps):

$|J_{(CH_3)2-4}| = 0.40$ $|J_{(CH_3)2-5}| = 0.40$ $|J_{(CH_3)3-4}| = 0.40$

$|J_{(CH_3)3-5}| = 0.40$ $|J_{(CH_3)2-(CH_3)3}| = 0.80$ $|J_{45}| = 1.80$

It is obviously not possible to assign each one of the two ring proton bands to a definite ring proton on the basis of the magnitudes of the observed couplings alone, nor is it possible to use the magnitudes for a structural assignment of the methyl group bands. By making use of empirical chemical shift correlations obtained from earlier studies of furans [14-16] one may, however, assign the low field ring proton band to hydrogen 5 and the low field methyl group band to the 2-methyl group with some confidence. As will be shown below this assignment is consistent with the observed signs of the couplings between the side-chain protons and the ring protons in this compound and with the known signs of the corresponding couplings in 2-methylfuran and 3-methylfuran. Finally it may be observed that the conclusion as to the sign of the $J_{(CH_3)2-(CH_3)3}$ spin coupling constant does not depend on the structural assignment, since the sign of $J_{(CH_3)2-(CH_3)3}$ is determined with respect to a side-chain to ring proton coupling J_{CH_3-H}, the sign of which is determined with respect to the ring coupling constant (cf. below). For convenience we shall however label the transitions in accordance with the assignments of Fig. 4.

A double resonance experiment was performed in which the 3-methyl group was selectively irradiated for the spin states $\pm \frac{1}{2}$ of the 2-methyl group and of the 4-hydrogen, while the 5-hydrogen spectrum was observed. The experiment was restricted to the transitions belonging to the $\pm \frac{1}{2}$ spin states of the 2-methyl group, because it is difficult to determine the optimum decoupling frequencies for the weaker quarters A1, A4, A5, and A8 belonging to the $\pm 3/2$ spin states of the 2-methyl groups (cf. Fig. 4). In this experiment we determined the sign of $J_{(CH_3)3-4}$ relative to that of the ring coupling J_{45} and $J_{(CH_3)2-(CH_3)3}$ relative that of $J_{(CH_3)2-5}$. The results are collected in Table 3 and some of the decoupled spectra are shown in Fig. 5. From the table it is obvious that $J_{(CH_3)3-4}$ is of opposite sign to J_{45}. This is in agreement with known signs of these coupling constants.[3] It is also found that the methyl-methyl coupling is of opposite sign to that of $J_{(CH_3)2-5}$. An analogous experiment with the 2-methyl group and the 4-hydrogen was also performed. The
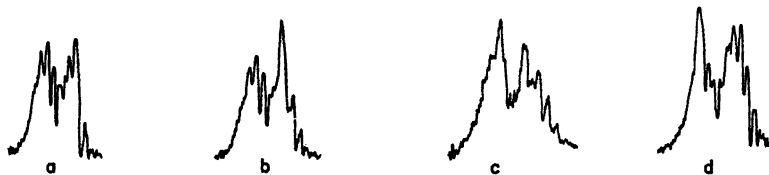

Fig. 5. The results of the double resonance experiments in 2,3-dimethylfuran; (a, b) show the 4-hydrogen band and (c, d) the 5-hydrogen band for selective decoupling of $J_{(CH_3)2-4}$ and $J_{(CH_3)3-5}$, respectively. The corresponding positions of the decoupling rf. field are indicated by arrows in Fig. 4a.

Table 3. The results of the decoupling of $J_{(CH_3)3-5}$ in 2,3-dimethylfuran.

Collapse of lines	Notation [a]	Predicted frequency differences (in cps)				Observed frequency differences (in cps)	Illustrated in figure
		$J_{45} \cdot J_{(CH_3)3-4} > 0$ $J_{23} \cdot J_{(CH_3)2-5} > 0$	$J_{45} \cdot J_{(CH_3)3-4} > 0$ $J_{23} \cdot J_{(CH_3)2-5} < 0$	$J_{45} \cdot J_{(CH_3)3-4} < 0$ $J_{23} \cdot J_{(CH_3)2-5} > 0$	$J_{45} \cdot J_{(CH_3)3-4} < 0$ $J_{23} \cdot J_{(CH_3)2-5} < 0$		
A2	$\Delta\nu_2$	−207.8	−208.6	−208.2	−209.0	−209.0	5d
A3	$\Delta\nu_3$	−208.2	−207.4	−208.6	−207.8	−207.9	5c
A6	$\Delta\nu_6$	−206.4	−207.2	−206.0	−206.8	−206.8	
A7	$\Delta\nu_7$	−206.8	−206.0	−206.4	−205.6	−205.3	
	$\Delta\nu_2 - \Delta\nu_3$	0.4	−1.2	0.4	−1.2	−1.1	
	$\Delta\nu_2 - \Delta\nu_6$	−1.4	−1.4	−2.2	−2.2	−2.2	
	$\Delta\nu_2 - \Delta\nu_7$	−1.0	−2.6	−1.8	−3.4	−3.7	

[a] The coupling $J_{(CH_3)2-(CH_3)3}$ has been denoted J_{23}.

Table 4. The results of the decoupling of $J_{(CH_3)2-4}$ in 2,3-dimethylfuran.

Collapse of lines	Notation [a]	Predicted frequency differences (in cps)				Observed frequency differences (in cps)	Illustrated in figure
		$J_{45} \cdot J_{(CH_3)2-5} > 0$ $J_{23} \cdot J_{(CH_3)3-4} > 0$	$J_{45} \cdot J_{(CH_3)2-5} > 0$ $J_{23} \cdot J_{(CH_3)3-4} < 0$	$J_{45} \cdot J_{(CH_3)2-5} < 0$ $J_{28} \cdot J_{(CH_3)3-4} > 0$	$J_{45} \cdot J_{(CH_3)2-5} < 0$ $J_{28} \cdot J_{(CH_3)3-4} < 0$		
M2	$\Delta\nu_2$	−156.2	−157.0	−156.6	−157.4	−157.2	5b
M3	$\Delta\nu_3$	−156.6	−155.8	−157.0	−156.2	−155.9	5a
M6	$\Delta\nu_6$	−154.8	−155.6	−154.4	−155.2	−154.8	
M7	$\Delta\nu_7$	−155.2	−154.4	−154.8	−154.0	−153.5	
	$\Delta\nu_2 - \Delta\nu_3$	0.4	−1.2	0.4	−1.2	−1.3	
	$\Delta\nu_2 - \Delta\nu_6$	−1.4	−1.4	−2.2	−2.2	−2.4	
	$\Delta\nu_2 - \Delta\nu_7$	−1.0	−2.6	−1.8	−3.4	−3.7	

[a] The coupling $J_{(CH_3)2-(CH_3)3}$ has been denoted J_{23}.

data are collected in Table 4 and some of the collapsed line patterns are depicted in Fig. 5. From Table 4 it is further confirmed that the assignment is correct since $J_{(CH_3)2-5}$ was found to be of opposite sign to that of the ring coupling.[3] Furthermore this result shows that $J_{(CH_3)2-(CH_3)3}$ (which is of opposite sign to $J_{(CH_3)2-5}$, cf. Table 3) is of the same sign as J_{45}. The table also shows that the methyl-methyl coupling carries the opposite sign to that of $J_{(CH_3)3-4}$, which in its turn is opposite to that of the ring coupling. We have made the most probable assignment for the 4- and 5-hydrogens, but it is obvious that the sign determination of the methyl-methyl coupling is not dependent on the assignment.

3.3. 3 - I o d o - 2,5 - d i m e t h y l f u r a n

The single resonance spectrum of a 42 % solution of 3-iodo-2,5-dimethyl-furan in cyclohexane at 40 and 60 Mcps is shown in Fig. 6 and appears as an AX_3Y_3 spectrum. The methyl groups do not give a strictly first order spectrum (shift difference 0.05 ppm), but the coupling constants given are obtained from a first order analysis since the coupling $J_{(CH_3)2-(CH_3)5}$ is only one fourth of the relative shift at 40 Mcps. It has been shown earlier that $J_{(CH_3)5-4}$ is considerably larger than $J_{(CH_3)2-4}$.[3,14,15] The high field methyl band shows the largest methyl coupling and is therefore assigned to the 5-methyl group. The coupling constants obtained are (in cps):

$$|J_{(CH_3)2-(CH_3)5}| = 0.55 \qquad |J_{(CH_3)2-4}| = 0.35 \qquad |J_{(CH_3)5-4}| = 1.05$$
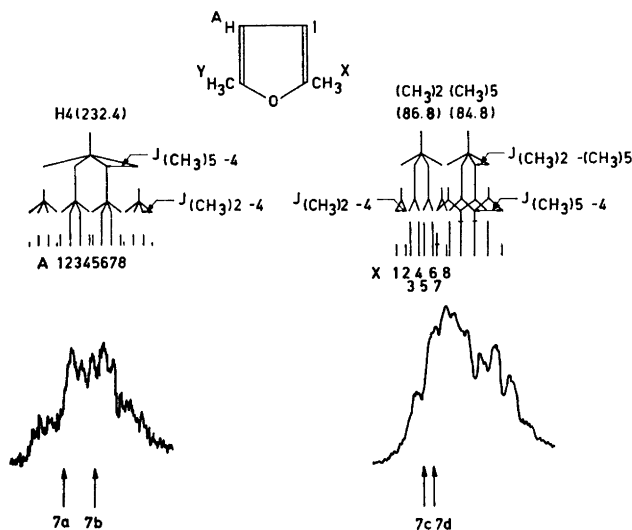

Fig. 6a. PMR spectrum at 40 Mcps of 3-iodo-2,5-dimethylfuran in a 42 % cyclohexane solution. The methyl band and the 4-hydrogen band have been recorded with different gain. The shifts are given relative to TMS as internal reference. Some of the lines have been numbered for future reference and the arrows refer to the double resonance experiments shown in Fig. 7.
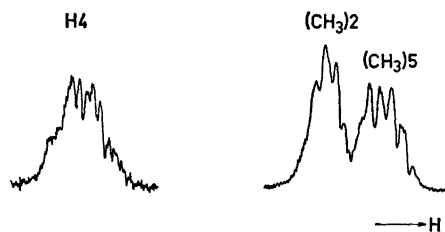
H4   (CH₃)2

(CH₃)5

———▸H

Fig. 6b. PMR spectrum at 60 Mcps of the same sample as in Fig. 6a.

In order to obtain the sign of $J_{(CH_s)2-(CH_s)5}$ we performed a double resonance experiment in which the 4-hydrogen was selectively decoupled for the spin states $\pm \frac{1}{2}$ of the 5-methyl group while recording the 2-methyl band. The reverse experiment was also done and the results of the two experiments are collected in Table 5. The corresponding figures are shown in Fig. 7. Irradiation of the 4-hydrogen while studying the 5-methyl band is not feasible and the same is true for the reverse experiment since $J_{(CH_s)5-4}$ is not much larger than $J_{(CH_s)2-4}$. Although the experimental optimum decoupling frequencies do not agree with those predicted for any sign alternative it is evident from a comparison between the predicted and observed frequency changes $\Delta \nu_{3,4} - \Delta \nu_{5,6}$ and $\Delta \nu_{1-4} - \Delta \nu_{5-8}$ that the results obtained are only consistent with the assumption that $J_{(CH_s)2-(CH_s)5}$ is of opposite sign to $J_{(CH_s)5-4}$. Since the latter coupling has previously been shown to be of opposite sign to that of the ring coupling [3] we conclude that the methyl-methyl coupling carries the same sign as the ring coupling. The rather big deviation of the experimental optimum decoupling frequencies from the predicted ones may partly be accounted for by second-order effects (≈ 0.2 cps) and an experimental uncertainty of approximately 0.4 cps in the first experiment and of approximately 0.3 cps in the second one. The frequency changes $\Delta \nu_{3,4} - \Delta \nu_{5,6}$ and $\Delta \nu_{1-4} - \Delta \nu_{5-8}$ are, however, less sensitive to second-order effects and to uncertainties in the chemical shift measurements and therefore a comparison of these observed entities with predicted ones is a better criterion.[6,13]
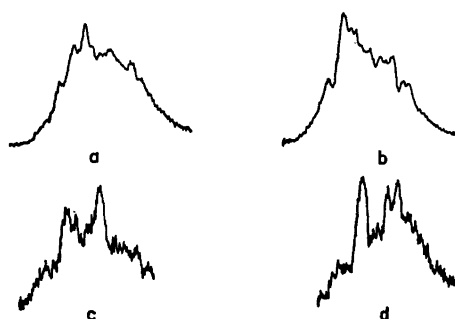
Fig. 7. Results of the double irradiation experiments in 3-iodo-2,5-dimethylfuran; (a, b) show the methyl band and (c, d) show the 4-hydrogen band in the presence of a selectively decoupling rf. field centered at the positions shown by the corresponding arrows in Fig. 6a.

a   b

c   d

Table 5. The results of the decoupling of $J_{(CH_3)2}-4$ in 3-iodo-2,5-dimethylfuran.

Collapse of lines	Notation	Predicted frequency differences (in cps)		Observed frequency differences (in cps)	Illustrated in figure
		$J_{(CH_3)5}-4\cdot J_{(CH_3)2\cdot(CH_3)5} > 0$	$J_{(CH_3)5}-4\cdot J_{(CH_3)2\cdot(CH_3)5} < 0$		
X3, X4	$\Delta\nu_{3,4}$	145.9	144.8	145.4	7b
X5, X6	$\Delta\nu_{5,6}$	145.4	146.4	147.0	7a
	$\Delta\nu_{3,4} - \Delta\nu_{5,6}$	0.5	−1.6	−1.6	
A1−A4	$\Delta\nu_{1-4}$	−145.9	−146.4	−145.8	7d
A5−A8	$\Delta\nu_{5-8}$	−145.4	−144.8	−144.2	7c
	$\Delta\nu_{1-4} - \Delta\nu_{5-8}$	−0.5	−1.6	−1.6	

4. DISCUSSION

The signs of the methyl-methyl couplings in two dimethylsubstituted furans and one disubstituted thiophene have been determined in this work. The signs of these couplings have in all cases been determined relative to those of ring proton-methyl couplings, the signs of which relative to that of the ring couplings were known. In all compounds studied here it is found that the methyl-methyl coupling carries the same sign as the ring couplings in thiophenes and furans (which are all positive [8,17-22]). The magnitude of $J_{(CH_3)2-(CH_3)5}$ in 3-iodo-2,5-dimethylfuran is $+ 0.55$ cps, which is the same value as for the methyl-methyl coupling in 3-acetyl-2,5-dimethyl thiophene.[2] If it is assumed that the methyl-methyl coupling is entirely π-electron transmitted [2,4,5,23,24] it follows that the π-electron contribution to the J_{CH_3-5} coupling in 2-methyl furan is approximately $- 0.55$ cps.[5,23,24] Since the observed J_{CH_3-5} coupling in 2-methylfuran is -0.40 cps [3] it may be suggested that the σ-electron contribution to this coupling is about $+ 0.15$ cps, which may be compared with the σ-electron contribution of $+ 0.40$ cps to J_{CH_3-5} in 3-nitro-2-methyl thiopene.[2] The conclusion that the σ-electron contribution to $J_{(CH_3)2-5}$ in thiophenes is larger than in furans is not entirely unreasonable since the ring coupling J_{25}, which is dominated by a σ-electron mechanism, is larger in thiophenes than in furans (3.2—3.7 and 1.40—1.65 cps, resp.).[9,14,16]

In 2,3-dimethylthiophene and 2,3-dimethylfuran the methyl-methyl couplings were found to be $+ 0.70$ and $+ 0.80$ cps. Together with the above mentioned fact that the 2-methyl-5-methyl couplings in 3-acetyl-2,5-dimethyl-thiophene and 3-iodo-2,5-dimethylfuran are of the same size, this indicates that the π-electron contributions to the proton-proton spin couplings in thiophenes and furans are of the same magnitude. Further support for this conclusion may be obtained from a study of the methyl-methyl couplings in 2,4-dimethylthiophene, 2,4-dimethylfuran, a 2-substituted 3,4-dimethylthiophene and a 2-substituted 3,4-dimethylfuran. In 2,3-dimethylthiophene and 2,3-dimethylfuran the methyl-methyl couplings are less than J_{CH_3-3} (or J_{CH_3-2}) in 2(or 3)-methylthiophenes and 2(or 3)-methylfurans. The σ-electron contributions (if any) to the couplings J_{CH_3-3} and J_{CH_3-2} will, however, according to the Dirac vector mode,[24,25] carry a negative sign, i.e. the same as the π-electron contribution. If the π-electron contribution to $J_{(CH_3)2-3}$ or $J_{(CH_3)3-2}$ in thiophenes and furans is approximately equal to minus the $J_{(CH_3)2-(CH_3)3}$ coupling, the σ-electron contribution can be estimated to be about -0.40 to -0.30 cps.

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