

## Signs of the Side-chain Spin Couplings in Furans

### II. 2-Methyl and 3-Methylfuran, 2-Furfurylidene malononitrile and N-(2-Furfurylidene)aniline

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The signs of the side-chain couplings in 2-methyl- and 3-methylfuran, 2-furfurylidene malononitrile and N-(2-furfurylidene)aniline have been determined relative to that of the ring couplings by the selective decoupling technique.

In 2-methylfuran only  $J_{\text{CH}_4}$  and in 3-methylfuran only  $J_{\text{CH}_3}$  have the same sign as the ring couplings.

In the 2-furfurylidene compounds the side-chain coupling to the 3-hydrogen is found to be of opposite sign to that of the ring couplings and the side-chain couplings to the 4- and 5-hydrogens are of the same sign as the ring couplings.

The relative signs are discussed in terms of  $\sigma$ - and  $\pi$ -electron contributions to the spin couplings.

#### 1. INTRODUCTION

In part I of this series we determined the signs of the long range aldehyde couplings in 2- and 3-furanaldehydes.<sup>1</sup> This work forms part of a survey of side-chain couplings in aromatic systems. In particular we are interested in comparing the couplings observed with different types of side-chains in a given aromatic system and also in comparing the couplings of a given side-chain in different aromatic compounds. In the present study we have supplemented our earlier study of substituted furans (Part I) with two types of side-chains with essentially  $sp^2$ -type hybridization of the  $\alpha$ -carbon, *viz.* 2-furfurylidene malononitrile and N-(2-furfurylidene)aniline. We have also studied the signs of the methyl couplings in 2- and 3-methylfurans which give us the possibility of comparing the side-chain methyl couplings in methylfurans and methylthiophenes.<sup>2,3</sup>

In the present investigation the selective decoupling double resonance method<sup>4-6</sup> was employed to determine the signs of the side-chain couplings relative to those of the ring couplings. In one case it was found expedient to employ the triple resonance technique described in part I.

## 2. EXPERIMENTAL

The 2-methyl- and 3-methylfurans were the same as used in an earlier investigation on substituted furans.<sup>7</sup> The 2-furfurylidene malonitrile was prepared through condensation of malodinitrile and 2-furaldehyde (*cf.* Ref. 8) and N-(2-furfurylidene)aniline was prepared according to de Chalmot.<sup>9</sup>

The spectra of 2-furfurylidene malonitrile were obtained using a Varian Associates model V 4300 B spectrometer operating at a radiofrequency of 40,000 Mcps. The spectra were recorded by use of phase sensitive detection by operating the Varian V 3521 integrator in the lower sideband mode. The single resonance spectra were calibrated using the sideband technique.

The other samples in the present investigation were studied at 60 Mcps. The single resonance spectra were obtained on a Varian model A 60 spectrometer operating at 60,007 Mcps, from which the shifts and couplings were evaluated. These spectra were calibrated using the side-band technique. The double resonance spectra were obtained using a Varian model V 4300 B (DP-60) spectrometer operating at 60,336 Mcps.

In the double resonance spectra the rf. field  $H_2$  of frequency  $\nu_2$  was obtained by frequency modulation of the rf. transmitter. The frequency of the measuring rf. field  $H_1$  is denoted  $\nu_1$ . 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 5512 A.

In the triple resonance experiment the strong rf. field  $H_3$  was produced by frequency modulation of the rf. transmitter, employing a Hewlett-Packard model 200 CD audio oscillator. The selective decoupling rf. field  $H_2$  was in this case produced by field modulation employing the Philips oscillator.

## 3. RESULTS

*3.1. 2-Methylfuran.* The single resonance spectrum at 60 Mcps of 2-methylfuran in a 33 % cyclohexane solution is shown in Fig. 1, and appears as an almost first order AKRX<sub>3</sub> spectrum, in which all groups are seen to couple with each other. The transitions have been numbered for future reference. The couplings are directly obtained from the corresponding splittings and are found to be (in cps):

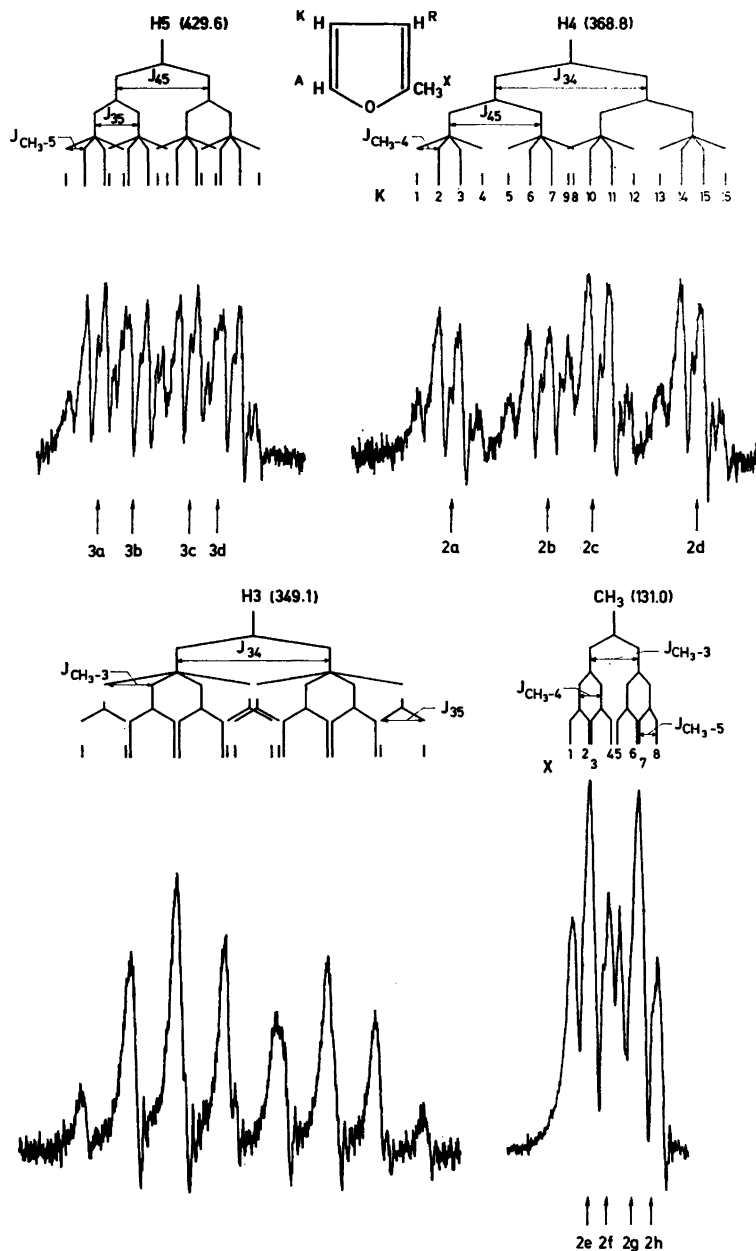
$$\begin{array}{l} |J_{34}| = 3.15 \quad |J_{35}| = 0.90 \quad |J_{45}| = 1.90 \\ |J_{\text{CH}_3-3}| = 1.00 \quad |J_{\text{CH}_3-4}| = 0.45 \quad |J_{\text{CH}_3-5}| = 0.40 \end{array}$$

These values agree well with those previously reported<sup>7,10</sup> at comparable resolution.

The 4-hydrogen band consists of four 1:3:3:1 quartets, which are well separated except for an overlap of one pair of lines (K8, K9). A double irradiation experiment in which the methyl coupling  $J_{\text{CH}_3-4}$  is decoupled by selective irradiation of these quartets may be easily performed. The simultaneous study of the collapsed patterns in the methyl band then gives the signs of the methyl couplings  $J_{\text{CH}_3-3}$  and  $J_{\text{CH}_3-5}$  relative to  $J_{34}$  and  $J_{45}$ , respectively. In these experiments the rf. amplitude was initially set low to ensure a selective irradiation.

Table 1. The results of the decoupling of  $J_{\text{CH}_3-4}$  in 2-methylfuran.

Collapse of lines	Notation	Predicted frequency differences (in cps)				Observed frequency difference (in cps)	Illustrated in figure
		$J_{34} \cdot J_{\text{CH}_3-3} > 0$ $J_{45} \cdot J_{\text{CH}_3-5} > 0$	$J_{34} \cdot J_{\text{CH}_3-3} > 0$ $J_{45} \cdot J_{\text{CH}_3-5} < 0$	$J_{34} \cdot J_{\text{CH}_3-3} < 0$ $J_{45} \cdot J_{\text{CH}_3-5} > 0$	$J_{34} \cdot J_{\text{CH}_3-3} < 0$ $J_{45} \cdot J_{\text{CH}_3-5} < 0$		
X1, X3	$\Delta\nu_{1,3}$	239.7	237.8	236.5	234.6	234.4	2 d
X2, X4	$\Delta\nu_{2,4}$	238.2	240.1	235.0	236.9	237.0	2 c
X5, X7	$\Delta\nu_{5,7}$	237.5	235.6	240.7	238.8	238.6	2 b
X6, X8	$\Delta\nu_{6,8}$	236.0	237.9	239.2	241.1	241.0	2 a
	$\Delta\nu_{1,3} - \Delta\nu_{2,4}$	1.5	-2.3	1.5	-2.3	-2.6	
	$\Delta\nu_{1,3} - \Delta\nu_{5,7}$	2.2	2.2	-4.2	-4.2	-4.2	
	$\Delta\nu_{1,3} - \Delta\nu_{6,8}$	3.7	-0.1	-2.7	-6.5	-6.6	
K1-K4	$\Delta\nu_{1-4}$	-239.7	-240.1	-240.7	-241.1	-241.1	2 h
K5-K8	$\Delta\nu_{5-8}$	-238.2	-237.8	-239.2	-238.8	-238.8	2 g
K9-K12	$\Delta\nu_{9-12}$	-237.5	-237.9	-236.5	-236.9	-237.0	2 f
K13-K16	$\Delta\nu_{13-16}$	-236.0	-235.6	-235.0	-234.6	-234.7	2 e
	$\Delta\nu_{1-4} - \Delta\nu_{5-8}$	-1.5	-2.3	-1.5	-2.3	-2.3	
	$\Delta\nu_{1-4} - \Delta\nu_{9-12}$	-2.2	-2.2	-4.2	-4.2	-4.1	
	$\Delta\nu_{1-4} - \Delta\nu_{13-16}$	-3.7	-4.5	-5.7	-6.5	-6.4	



*Fig. 1.* PMR spectrum at 60.007 Mcps of 2-methylfuran in a 33 % cyclohexane solution. The methyl band has been recorded with reduced gain. The shifts are given relative to TMS as internal reference for a proton resonance frequency of 60.336 Mcps, which was employed in the double irradiation experiments. The arrows refer to the centering of the decoupling rf. field in the double irradiation experiments shown in Figs. 2 and 3.

tion, and then increased until easily recognizable collapsed patterns were obtained, but still kept low enough to permit an accurate determination of the optimum decoupling frequencies ( $\pm 0.3$  cps).

The results of these experiments are collected in Table 1, where the lines collapsed in an experiment are given, together with the measured optimum decoupling frequencies  $\nu_2 - \nu_1$ , as well as the differences<sup>1</sup> between these optimum values of  $\nu_2 - \nu_1$ . The predicted decoupling frequencies for the different sign alternatives calculated from the known magnitudes of shifts and couplings, are also given in the table.

From the measured optimum decoupling frequencies it is clear that  $J_{\text{CH}_3,3}$  is of opposite sign to  $J_{34}$  and that  $J_{\text{CH}_3,5}$  is of opposite sign to  $J_{45}$ . Since it has been shown that the signs of all proton ring couplings in the furans are the same,<sup>5,11</sup> it can be concluded that both methyl couplings  $J_{\text{CH}_3,3}$  and  $J_{\text{CH}_3,5}$  are of the same sign, *i.e.* opposite to that of the ring couplings. The reverse experiment was also performed, *i.e.* selective irradiation in the methyl band while studying the 4-hydrogen spectrum. In this experiment the amplitude of the irradiating rf. field  $H_2$  could be kept lower than in the previous case.<sup>12,13</sup> The optimum decoupling frequencies could in this case be determined to within  $\pm 0.1$  cps. The decoupling frequencies predicted for the different sign alternatives in this latter series of experiments do not differ as markedly as in the former series, but with the higher precision attainable there is still no ambiguity in the interpretation of the results. The results of these experiments are included in Table 1, and it is confirmed that the methyl couplings  $J_{\text{CH}_3,3}$  and  $J_{\text{CH}_3,5}$  are both of opposite sign to the ring couplings.

The spectra obtained in the experiments reported in Table 1 are depicted in Fig. 2.

The 5-hydrogen band consists of four partly overlapping 1:3:3:1 quartets (see Fig. 1), but a decoupling of  $J_{\text{CH}_3,5}$  by irradiation of these quartets while studying the collapses of related lines in the methyl band may still be successfully performed. The results of this experiment are collected in Table 2. The corresponding collapsed patterns are displayed in Fig. 3.

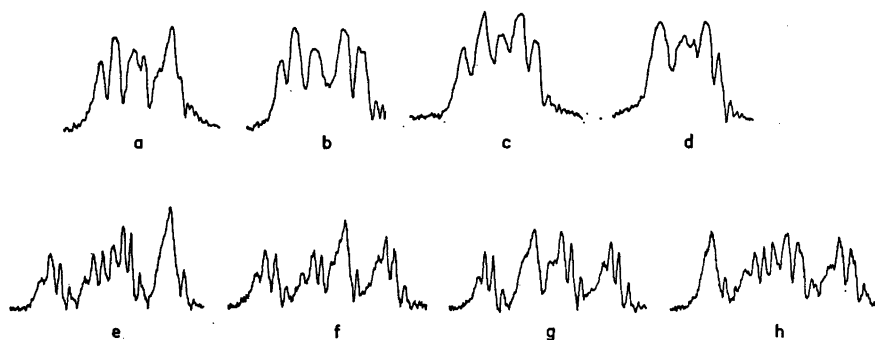


Fig. 2. Results of the double irradiation experiments in 2-methyl-furan; (a–d) show the methyl band and (e–h) the 4-hydrogen band for selective decoupling of  $J_{\text{CH}_3,4}$ . The corresponding positions of the decoupling rf. field are indicated by arrows in Fig. 1.

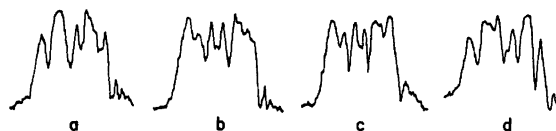


Fig. 3. The results of the selective decoupling of  $J_{\text{CH}_3-5}$  in 2-methylfuran; (a–d) show the methyl band when the strong rf. field is centered at the corresponding positions indicated by arrows in Fig. 1.

Depending on the small differences between the predicted optimum decoupling frequencies for different sign alternatives and the magnitude of the splittings to be decoupled, it was found necessary to compromise between the requirements of a low  $H_2$  amplitude for good selectivity and a high  $H_2$  amplitude for perfect collapses. An additional complication in the interpretation of the decoupled methyl patterns is that in a field sweep experiment the optimum collapse of  $X_1$ ,  $X_2$  is accompanied by a partial collapse of  $X_7$ ,  $X_8$  or *vice versa* (see Fig. 3), due to the small difference between the optimum decoupling frequencies for these splittings.

From Table 2 it is found that  $J_{\text{CH}_3-4}$  carries the same sign as  $J_{45}$  and that  $J_{\text{CH}_3-3}$  is of opposite sign to  $J_{35}$ . This latter result is in agreement with that of the previous experiments (Table 1).

3.2. *3-Methylfuran*. The single resonance spectrum at 60 Mcps of 3-methylfuran in a 34 % cyclohexane solution is shown in Fig. 4. This compound shows an almost first order AKRX<sub>3</sub> spectrum in which all groups couple to each other. The 40 Mcps spectrum reported earlier<sup>7</sup> was not analysed completely.

In the well resolved 60 Mcps spectrum of Fig. 4, however, a complete assignment can be made. The third order perturbation corrections<sup>14</sup> are negligible and the couplings are directly obtained from the corresponding splittings in the spectrum. The couplings are (in cps):

$$\begin{array}{l} |J_{45}| = 1.80 \quad |J_{25}| = 1.55 \quad |J_{24}| = 0.90 \\ |J_{\text{CH}_3-2}| = 1.20 \quad |J_{\text{CH}_3-4}| = 0.45 \quad |J_{\text{CH}_3-5}| = 0.40 \end{array}$$

The 5-hydrogen band consists of four 1:3:3:1 quartets, two of which are strongly overlapping due to the small difference between  $J_{25}$  and  $J_{45}$ . Selective decoupling of  $J_{\text{CH}_3-5}$  by irradiation of the low and high field quartets in this band can easily be performed, however, and should lead to clear collapses of related lines in the methyl band. Decoupling by irradiation of the overlapping quartets cannot be done as selectively and was not performed. The results of the experiments described are given in Table 3 and the corresponding spectra are reproduced in Fig. 5. It is seen from the table that the observed optimum decoupling frequencies are only consistent with the assumption that  $J_{\text{CH}_3-2}$  and  $J_{\text{CH}_3-4}$  are both opposite in sign to the ring couplings.

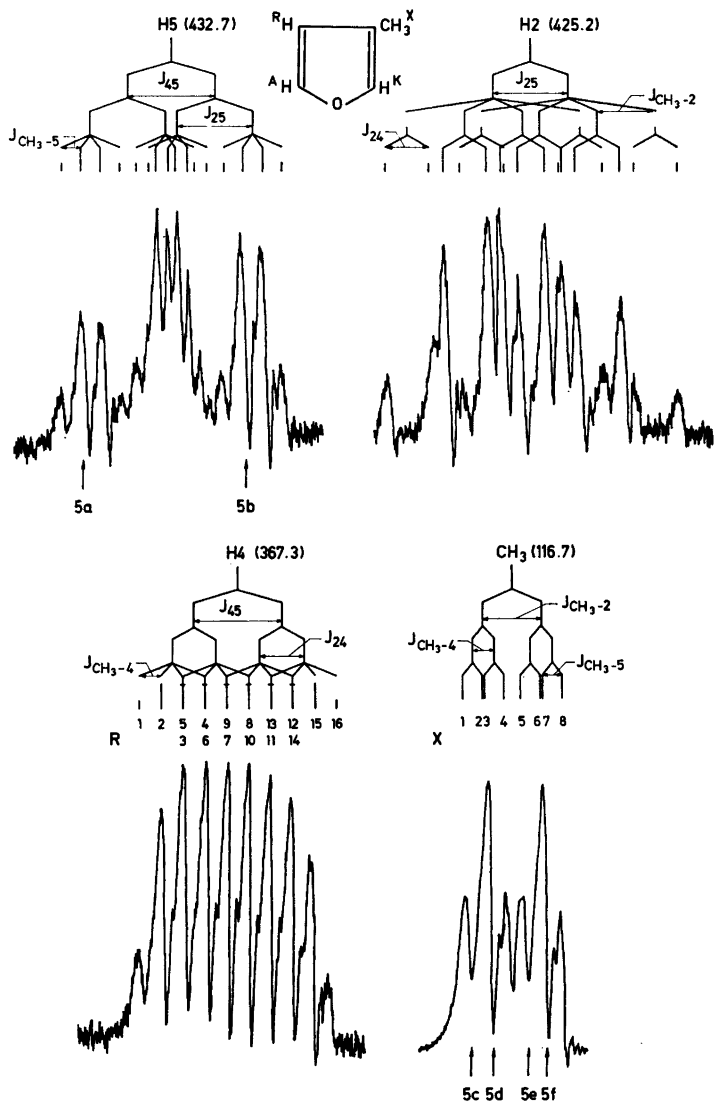
To obtain the sign of  $J_{\text{CH}_3-5}$  it is feasible to decouple  $J_{\text{CH}_3-4}$  by irradiation in the methyl band while studying the 4-hydrogen band. The 4-hydrogen band consists of four overlapping 1:3:3:1 quartets, and the decoupling of  $J_{\text{CH}_3-4}$  for given values of the 2- and 5-hydrogen spin states should lead to collapse of a related quartet.

Table 2. The results of the decoupling of  $J_{\text{CH}_{3-5}}$  in 2-methylfuran.

Collapse of lines	Notation	Predicted frequency differences (in cps)		Observed frequency difference (in cps)	Illustrated in figure
		$J_{36} \cdot J_{\text{CH}_{3-3}} > 0$ $J_{45} \cdot J_{\text{CH}_{3-4}} > 0$	$J_{35} \cdot J_{\text{CH}_{3-3}} > 0$ $J_{45} \cdot J_{\text{CH}_{3-4}} > 0$		
X1, X2	$\Delta\nu_{1,2}$	299.3	297.4	298.4	298.4
X3, X4	$\Delta\nu_{3,4}$	297.8	299.8	296.9	297.1
X5, X6	$\Delta\nu_{5,6}$	299.4	297.5	300.3	300.2
X7, X8	$\Delta\nu_{7,8}$	297.9	299.9	298.8	298.7
	$\Delta\nu_{1,2} - \Delta\nu_{3,4}$	1.5	-2.4	1.5	1.3
	$\Delta\nu_{1,2} - \Delta\nu_{5,6}$	-0.1	-0.1	-1.9	-1.8
	$\Delta\nu_{1,2} - \Delta\nu_{7,8}$	1.4	-2.5	-0.4	-0.3
				296.5	3 b
				298.9	3 d
				298.4	3 a
				300.8	3 c

Table 3. The results of the decoupling of  $J_{\text{CH}_{3-5}}$  and  $J_{\text{CH}_{3-4}}$ , respectively, in 3-methylfuran.

Collapse of lines	Notation	Predicted frequency differences (in cps)		Observed frequency difference (in cps)	Illustrated in figure
		$J_{45} \cdot J_{\text{CH}_{3-4}} > 0$ $J_{25} \cdot J_{\text{CH}_{3-2}} > 0$	$J_{45} \cdot J_{\text{CH}_{3-4}} > 0$ $J_{25} \cdot J_{\text{CH}_{3-2}} > 0$		
X1, X2	$\Delta\nu_{1,2}$	316.8	315.2	315.0	313.5
X7, X8	$\Delta\nu_{7,8}$	315.0	316.6	316.8	318.6
	$\Delta\nu_{1,2} - \Delta\nu_{7,8}$	1.8	-1.4	-1.8	-5.0
				313.4	5 b
				318.4	5 a
				-5.0	
R1-R4	$\Delta\nu_{1-4}$	-251.1	-252.3	-251.5	-252.3
R5-R8	$\Delta\nu_{5-8}$	-251.4	-250.2	-251.8	-250.2
R9-R12	$\Delta\nu_{9-12}$	-249.7	-250.9	-249.3	-250.9
R13-R16	$\Delta\nu_{13-16}$	-250.0	-248.8	-249.6	-248.8
	$\Delta\nu_{1-4} - \Delta\nu_{5-8}$	0.3	-2.1	0.3	-2.1
	$\Delta\nu_{1-4} - \Delta\nu_{9-12}$	-1.4	-1.4	-2.2	-1.4
	$\Delta\nu_{1-4} - \Delta\nu_{13-16}$	-1.1	-3.5	-1.9	-3.5
				-252.7	5 e
				-250.6	5 c
				-250.5	5 f
				-248.4	5 d



*Fig. 4.* PMR spectrum at 60.007 Mcps of 3-methylfuran in a 34% cyclohexane solution. The methyl band has been recorded with reduced gain. The shifts are given relative to TMS as internal reference for a proton resonance frequency of 60.336 Mcps, which was employed in the double irradiation experiment. The arrows refer to the centering of the decoupling rf. field in the double irradiation experiments shown in Fig. 5.



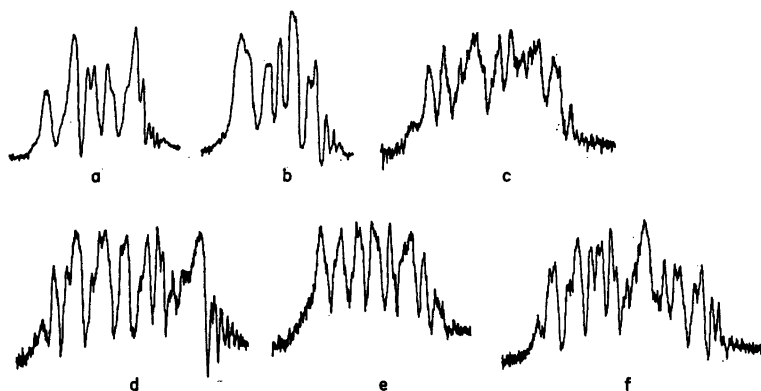


Fig. 5. The results of the double irradiation experiments in 3-methylfuran; (a,b) show the methyl band and (c-f) show the 4-hydrogen band in the presence of a selective decoupling rf. field centered at the positions shown by the corresponding arrows in Fig. 4.

In the reverse experiment, a larger irradiating amplitude will be necessary to produce nice collapses in the methyl band. Due to the strong overlapping of the 1:3:3:1 quartets the irradiation can then not be applied selectively, and these experiments were not attempted.

The results of the decoupling experiments are given in Table 3 and the corresponding spectra are depicted in Fig. 5. As seen from Fig. 5, one obtains a perturbation of the quartet R9, R10, R11, R12 for the optimum decoupling of R5, R6, R7, R8 and *vice versa*. This is due to the small difference in optimum decoupling frequency for these quartets (*cf.* Table 3).

From the measured optimum decoupling frequencies it is found that  $J_{\text{CH}_4-5}$  is of the same sign as  $J_{45}$ . It is also confirmed that  $J_{\text{CH}_4-2}$  is of opposite sign to the ring couplings.

**3.3 2-Furfurylidenemalononitrile.** The single resonance spectrum at 40 Mcps of a 10 % solution of 2-furfurylidenemalononitrile in a mixture of acetone and carbon tetrachloride is shown in Fig. 6. This compound gives a first order AKRX spectrum, where all protons couple to each other. In the analysis of the spectrum, the magnitudes of the ring couplings reported earlier<sup>7,15</sup> were employed to obtain the correct assignment of the various bands. A first order analysis gives the following coupling constants (in cps):

$$\begin{array}{lll} |J_{34}| = 3.75 & |J_{35}| = 0.70 & |J_{45}| = 1.65 \\ |J_{\text{H}\alpha-3}| = 0.40 & |J_{\text{H}\alpha-4}| = 0.40 & |J_{\text{H}\alpha-5}| = 0.50 \end{array}$$

The signs of the side-chain couplings  $J_{\text{H}\alpha-4}$  and  $J_{\text{H}\alpha-5}$  can be determined relative to that of the ring couplings in a double irradiation experiment with decoupling of  $J_{\text{H}\alpha-4}$ . This decoupling can be performed either by irradiation in the 4-hydrogen band while studying the  $\text{H}\alpha$  band or *vice versa*. The strong overlapping of the lines to be collapsed in the  $\text{H}\alpha$  band makes the determination of the optimum decoupling frequencies more difficult in this decoupling

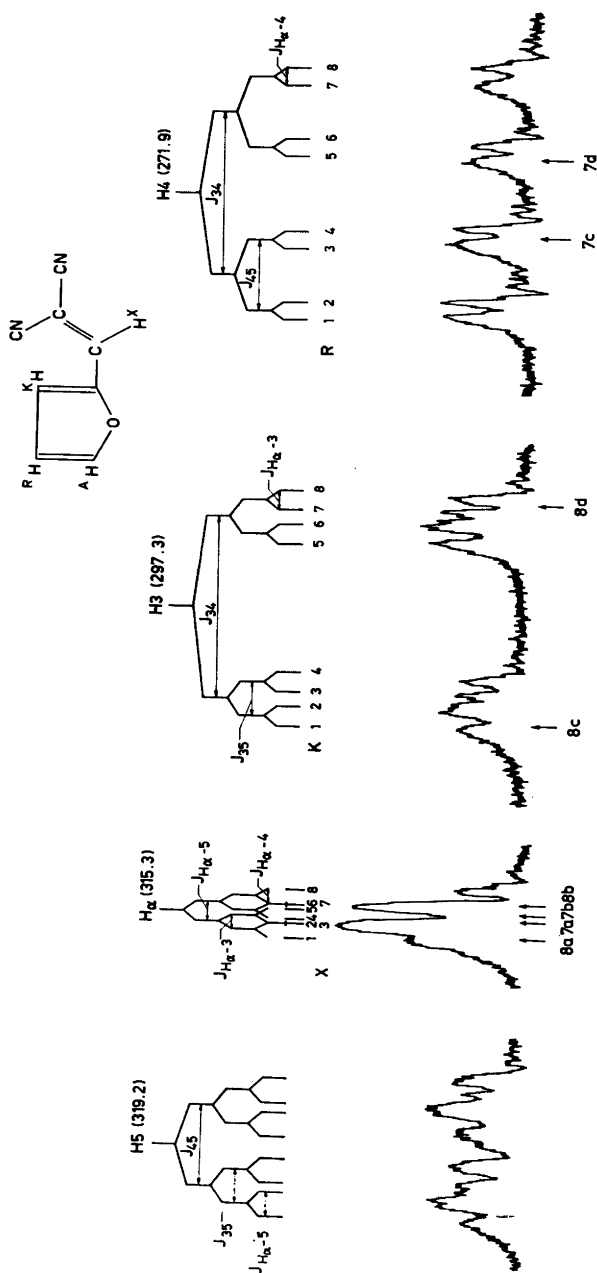


Fig. 6. The single resonance spectrum at 40 Mcps of a 10 % solution of 2-furfurylidene malonitrile in a mixture of acetone and carbon tetrachloride (proportions 1:3). The side-chain proton has been designated H $\alpha$ . The shifts are given relative to TMS as internal reference. The arrows refer to the centering of the decoupling rf. field in the double irradiation experiments shown in Figs. 7 and 8.

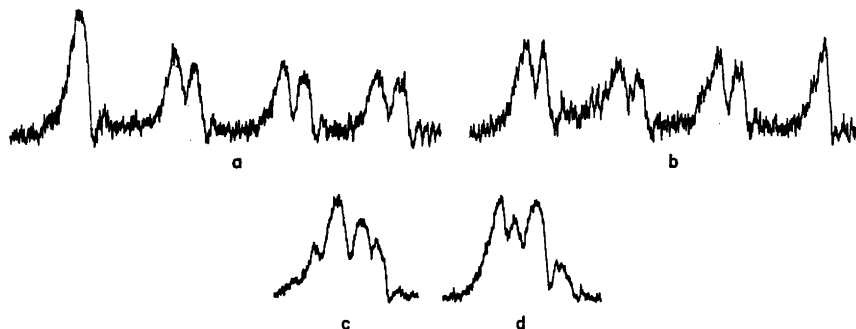


Fig. 7. Results of the double irradiation experiments in 2-furfurylidene malonitrile; (a, b) show the 4-hydrogen band and (c, d) the side-chain hydrogen band for selective decoupling of  $J_{H\alpha-4}$ . The corresponding positions of the decoupling rf. field are indicated by arrows in Fig. 6.

experiment, than in the reverse experiment where the doublets to be collapsed in the 4-hydrogen band are all well separated. The differences between the decoupling frequencies predicted for different sign alternatives are larger, however, in the former experiment.

Both experiments were performed and the results are collected in Table 4. Some of the collapsed line patterns corresponding to the entries in the table are depicted in Fig. 7.

It is seen from the table that the resulting optimum decoupling frequencies are only consistent with the assumption that  $J_{H\alpha-3}$  carries the opposite sign to that of the ring couplings, while  $J_{H\alpha-5}$  is of the same sign as the ring couplings.

The sign of  $J_{H\alpha-4}$  can be obtained by decoupling of  $J_{H\alpha-3}$  by selective irradiation in the  $H\alpha$  band while recording the collapses of related doublets in

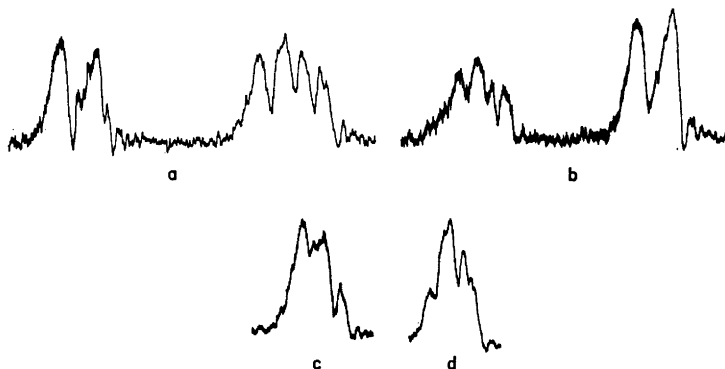


Fig. 8. Results of the double irradiation experiments in 2-furfurylidene malonitrile; (a, b) show the 3-hydrogen band and (c, d) the  $H\alpha$ -hydrogen band for selective decoupling of  $J_{H\alpha-3}$ . The corresponding positions of the decoupling rf. field are indicated by arrows in Fig. 6.

Table 4. The results of the decoupling of  $J_{\text{H}\alpha-4}$  in 2-furfurylidene malononitrile.

Collapse of lines	Notation	Predicted frequency differences (in cps)		Observed frequency difference (in cps)	Illustrated in figure
		$J_{45} \cdot J_{\text{H}\alpha-5} > 0$	$J_{34} \cdot J_{\text{H}\alpha-3} > 0$		
R1, R2	$\Delta\nu_{1,2}$	41.2	40.7	40.8	7 a
R3, R4	$\Delta\nu_{3,4}$	42.4	42.9	42.0	
R5, R6	$\Delta\nu_{5,6}$	44.6	44.1	44.5	7 b
R7, R8	$\Delta\nu_{7,8}$	45.8	46.3	46.2	
	$\Delta\nu_{1,2} - \Delta\nu_{3,4}$	-1.2	-2.2	-1.2	
	$\Delta\nu_{1,2} - \Delta\nu_{5,6}$	-3.4	-3.4	-4.2	
	$\Delta\nu_{1,2} - \Delta\nu_{7,8}$	-4.6	-5.6	-5.3	
X1, X2	$\Delta\nu_{1,2}$	-41.2	-42.9	-44.8	7 d
X3, X5	$\Delta\nu_{3,5}$	-44.6	-46.3	-40.7	
X4, X6	$\Delta\nu_{4,6}$	-42.4	-40.7	-46.2	7 c
X7, X8	$\Delta\nu_{7,8}$	-45.8	-44.1	-42.0	
	$\Delta\nu_{1,2} - \Delta\nu_{3,5}$	3.4	3.4	-4.1	
	$\Delta\nu_{1,2} - \Delta\nu_{4,6}$	1.2	-2.2	1.4	
	$\Delta\nu_{1,2} - \Delta\nu_{7,8}$	4.6	1.2	-2.8	

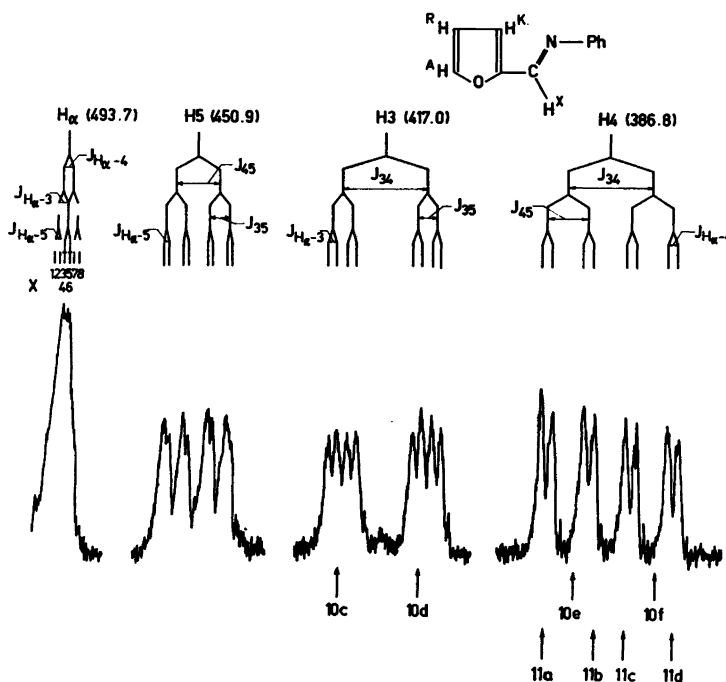
Table 5. The results of the decoupling of  $J_{\text{H}\alpha-3}$  in 2-furfurylidene malononitrile.

Collapse of lines	Notation	Predicted frequency differences (in cps)		Observed frequency difference (in cps)	Illustrated in figure
		$J_{35} \cdot J_{\text{H}\alpha-5} > 0$	$J_{34} \cdot J_{\text{H}\alpha-4} > 0$		
K1, K2	$\Delta\nu_{1,2}$	16.2	15.7	16.2	8 a
K3, K4	$\Delta\nu_{3,4}$	16.4	16.9	16.4	
K5, K6	$\Delta\nu_{5,6}$	19.4	18.9	19.4	8 b
K7, K8	$\Delta\nu_{7,8}$	19.6	20.1	19.7	
	$\Delta\nu_{1,2} - \Delta\nu_{3,4}$	-0.2	-1.2	-0.2	
	$\Delta\nu_{1,2} - \Delta\nu_{5,6}$	-3.2	-3.2	-3.2	
	$\Delta\nu_{1,2} - \Delta\nu_{7,8}$	-3.4	-4.4	-3.5	
X1, X3	$\Delta\nu_{1,3}$	-16.2	-16.9	-16.1	8 c
X6, X8	$\Delta\nu_{6,8}$	-19.6	-18.9	-19.7	
	$\Delta\nu_{1,3} - \Delta\nu_{6,8}$	3.4	2.0	3.6	

the 3-hydrogen band. The results of these experiments are summarized in Table 5. Some of the corresponding spectra are depicted in Fig. 8. Due to the small difference between the decoupling frequencies for optimum collapse of the doublets K1, K2 and K3, K4, respectively, (0.2 cps), a partial collapse of one of these doublets is obtained when the other shows optimum collapse. The same phenomenon occurs in the decoupling of the other doublet pairs K5, K6 and K7, K8.

The experimental optimum decoupling frequencies and their differences agree only with those calculated under the assumption that  $J_{H\alpha-4}$  and  $J_{H\alpha-5}$  carry the same sign as the ring couplings. These frequencies differ from those predicted for other sign alternatives by only 1 cps. The sign determination is quite unambiguous, however, since the uncertainty in the experimental frequencies is estimated to be less than 0.3 cps.

A confirmation of the result can be obtained from the reverse experiment. In this experiment only collapses of the outermost doublets X1, X3 and X6, X8 were produced, which are most easily identified. The results of this experiment are included in Table 5 and the corresponding spectra are displayed in



*Fig. 9.* PMR spectrum at 60.007 Mcps of N-(2-furfurylidene)aniline in a 10 % carbon tetrachloride solution. The side-chain hydrogen is denoted by H $\alpha$  and the phenyl ring by Ph. The shifts are given relative to TMS as internal reference for a proton resonance frequency of 60.336 Mcps, which was employed in double irradiation experiments. The arrows refer to the centering of the decoupling rf. field in the irradiation experiments shown in Figs. 10 and 11.

Fig. 8. This experiment also shows that  $J_{H\alpha-4}$  and  $J_{H\alpha-5}$  are of the same sign as the ring couplings.

3.4. *N*-(2-Furfurylidene)aniline. The single resonance spectrum at 60 Mcps of *N*-(2-furfurylidene)aniline in a 10 % solution in carbon tetrachloride is shown in Fig. 9. The spectrum reveals that only one of the two possible (*cis-trans*) isomers is present in appreciable quantity, but a decision as to which isomer is present cannot be made from this spectrum. The *trans* structure drawn is only tentative. This compound gives a first order AKRX spectrum in which all protons couple to each other. The magnitudes of the ring couplings in furans reported earlier<sup>7,15</sup> were used as a basis for the assignment of the different bands. The coupling constants obtained are (in cps):

$$\begin{array}{lll} |J_{34}| = 3.50 & |J_{35}| = 0.80 & |J_{45}| = 1.75 \\ |J_{H\alpha-3}| = 0.35 & |J_{H\alpha-4}| = 0.40 & |J_{H\alpha-5}| = 0.20 \end{array}$$

The  $H\alpha$  band, which is displaced towards lowest field, is actually composed of eight lines, but appears as one broad unresolved line (*cf.* Fig. 10a). To determine the signs of the side-chain couplings relative to that of the ring couplings, it is preferable to selectively irradiate in the ring proton bands and study the collapsed patterns in the side-chain hydrogen band.

The interpretation of the reverse experiments will not be unambiguous since the differences between the optimum decoupling frequencies predicted for different sign alternatives are of the same magnitude as the uncertainty in the experimentally obtained frequencies.

Due to the strong overlap of the lines in the  $H\alpha$  band, an identification of collapsed lines and a determination of the optimum decoupling frequencies is difficult. The appearance of the  $H\alpha$  band can, however, be simplified by applying a triple resonance technique.

In this triple resonance experiment a third rf. field  $H_3$  of frequency  $\nu_3$  was centered at the 5-hydrogen band, and the 5-proton was effectively decoupled from the remaining spin system. The  $H\alpha$  band will then appear as a 1:2:1 triplet as is shown in Fig. 10b. A selective decoupling experiment can now be performed as in an ordinary three spin system.<sup>1</sup> Decoupling of  $J_{H\alpha-3}$  by selective irradiation in the 3-hydrogen band while studying the  $H\alpha$  band will

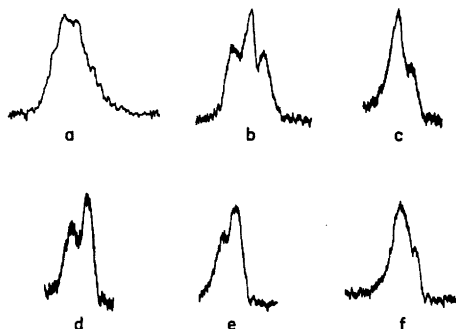


Fig. 10. The results of the triple resonance experiments in *N*-(2-furfurylidene)aniline; (a) shows the single resonance spectrum of the  $H\alpha$  hydrogen; (b) shows the  $H\alpha$  band in the presence of a strong rf. field  $H_3$  centered at the 5 hydrogen to decouple this proton completely from the rest of the spin system; (c-f) show the  $H\alpha$  band in the presence of a selective decoupling field (in addition to the strong rf. field  $H_3$ ) centered at the positions shown by the corresponding arrows in Fig. 9.

Table 6. The results of the triple resonance experiments on N-(2-furfurylidene)aniline. Complete decoupling of the 5-hydrogen, combined with selective decoupling of  $J_{\text{H}\alpha-3}$  and  $J_{\text{H}\alpha-4}$ , respectively.

Collapse of lines	Notation	Predicted frequency differences (in cps)		Observed frequency difference (in cps)	Illustrated in figure
		$J_{34} \cdot J_{\text{H}\alpha-4} > 0$	$J_{34} \cdot J_{\text{H}\alpha-4} < 0$		
X1', X2'	$\Delta\nu_{1,2}$	-75.1	-78.6	-74.9	10 c
X3', X4'	$\Delta\nu_{3,4}$	-78.2	-74.7	-77.7	10 d
	$\Delta\nu_{1,2} - \Delta\nu_{3,4}$	3.1	-3.9	2.8	
		$J_{34} \cdot J_{\text{H}\alpha-3} > 0$	$J_{34} \cdot J_{\text{H}\alpha-3} < 0$		
X1', X3'	$\Delta\nu_{1,3}$	-105.3	-108.8	-108.9	10 f
X2', X4'	$\Delta\nu_{2,4}$	-108.4	-104.9	-105.1	10 e
	$\Delta\nu_{1,3} - \Delta\nu_{2,4}$	3.1	-3.9	-3.8	

then give the sign of  $J_{\text{H}\alpha-4}$  relative to that of  $J_{34}$ , and decoupling of  $J_{\text{H}\alpha-4}$  will correspondingly give the sign of  $J_{\text{H}\alpha-3}$ .

The results of these triple resonance experiments are given in Table 6. The optimum decoupling frequencies in this table could not be determined to better than 0.5 cps, which in this case is more than sufficient to distinguish between the different sign alternatives. It is seen that  $J_{\text{H}\alpha-4}$  is of the same sign as  $J_{34}$ , while  $J_{\text{H}\alpha-3}$  is of opposite sign to the ring couplings. The spectra corresponding to the entries in Table 6 are depicted in Fig. 10 (c-f.).

To determine the sign of  $J_{\text{H}\alpha-5}$  it was similarly attempted to perform a triple resonance experiment with a complete decoupling of the 3-hydrogen (or 4-hydrogen) band from the remaining spin system. However, it was found experimentally difficult to achieve a complete decoupling of these hydrogens because of the largeness of the  $J_{34}$  coupling.

Instead, an ordinary double resonance experiment was performed in which  $J_{\text{H}\alpha-4}$  was decoupled by selective irradiation in the 4-hydrogen band, with a simultaneous study of the H $\alpha$  multiplet. The optimum decoupling frequencies could not be determined as in the preceding experiments by a stepwise change

Table 7. The results of the decoupling of  $J_{\text{H}\alpha-4}$  in N-(2-furfurylidene)aniline.

Collapse of lines	Predicted frequency differences (in cps)				Observed frequency difference (in cps)	Illustrated in figure
	$J_{34} \cdot J_{\text{H}\alpha-3} > 0$	$J_{34} \cdot J_{\text{H}\alpha-3} > 0$	$J_{34} \cdot J_{\text{H}\alpha-3} < 0$	$J_{34} \cdot J_{\text{H}\alpha-3} < 0$		
X1, X4	-104.6	-106.3	-108.1	-109.8	-107.8	11 c
X2, X6	-106.1	-104.4	-109.6	-107.9	-109.6	11 d
X3, X7	-107.7	-109.4	-104.2	-105.9	-104.0	11 a
X5, X8	-109.2	-107.5	-105.7	-104.0	-105.8	11 b

in modulating frequency. The decoupling frequency was instead set at the frequencies predicted for different sign alternatives of the couplings and the patterns obtained in the  $H\alpha$  band were studied. It was found that recognizably collapsed patterns were obtained only for the decoupling frequencies calculated under the assumption that  $J_{H\alpha-5}$  carries the same sign as  $J_{45}$ , and that  $J_{H\alpha-3}$  is of opposite sign to  $J_{34}$ . These spectra are reproduced in Fig. 11 and the frequencies are given in Table 7.

Fig. 11c shows the collapse of X1, X4 and Fig. 11b the collapse of X5, X8. The weak outer lines, X1 and X8, respectively, have disappeared and an almost resolved sharp peak is obtained at the positions of the collapsed lines (at X2 and X7, respectively) where the collapsed lines are positioned.



Fig. 11. The results of the double resonance experiments in N-(2-furfurylidene)aniline (a–d) show the  $H\alpha$  band for selective decoupling of  $J_{H\alpha-4}$ . The corresponding positions of the decoupling field are indicated by arrows in Fig. 9.

Fig. 11d shows the collapse of lines X2 and X6. In this case a sharp peak is obtained at the positions of the X3, X4 lines, and the earlier unresolved flank line X1 is now resolvable. Fig. 11a similarly shows the collapse of X3, X7, where the flank line X8 is now well resolved.

Although unambiguous conclusions cannot be drawn from one of these spectra alone, the whole series of decoupled patterns unambiguously shows that  $J_{H\alpha-5}$  is of the same sign as the ring couplings.

Table 8. Side-chain couplings in furans. Couplings (in cps)

	sign	$J_{CH_3-3}$ magnitude <sup>a</sup>	sign	$J_{CH_3-3}$ magnitude <sup>a</sup>	sign	$J_{CH_3-4}$ magnitude <sup>a</sup>	sign	$J_{CH_3-5}$ magnitude <sup>a</sup>
2-methylfuran	—	1.20	—	1.00	+	0.45	—	0.40
3-methylfuran	—	1.20	—	1.00	—	0.45	+	0.40
	sign	$J_{H\alpha-3}$ magnitude <sup>a</sup>	sign	$J_{H\alpha-3}$ magnitude <sup>a</sup>	sign	$J_{H\alpha-4}$ magnitude <sup>a</sup>	sign	$J_{H\alpha-5}$ magnitude <sup>a</sup>
2-furfurylidene- malononitrile	—	0.40	+	0.40	+	0.40	+	0.50
N-(2-furfurylidene)- aniline	—	0.35	+	0.40	+	0.40	+	0.20

<sup>a</sup> All values are estimated to be accurate to within  $\pm 0.10$  cps.



## 4. DISCUSSION

The side-chain couplings studied in the present work are summarized in Table 8 where both the magnitudes and the signs are listed. The signs are given relative to that of the ring couplings in furans, which is most likely the same as that of the *ortho* coupling in benzenes. The absolute sign of the latter coupling has been shown to be positive.<sup>16</sup>

The signs of the couplings between the side-chain proton and the 4- and 5-protons in 2-furfurylidene malononitrile and N-(2-furfurylidene)aniline are both positive. This is the same sign as  $J_{\text{CHO-4}}$  and  $J_{\text{CHO-5}}$  in 2-furaldehyde.<sup>1</sup> This result is not unexpected in view of the fact that the framework within which the side-chain couplings are transmitted is similar in these three compounds. The coupling between the side-chain and the 3-hydrogen is of similar magnitude to the coupling between the side-chain and the 4-hydrogen in the two compounds studied here, in contrast to the case of 2-furaldehyde where this coupling is unobservably small (less than 0.15 cps). The negative sign observed for this coupling is in agreement with the prediction based on the Dirac vector model.<sup>17,18</sup> The magnitude of the spin coupling between the side-chain and the 5-proton in N-(2-furfurylidene)aniline is much smaller than the corresponding coupling in 2-furaldehyde and in 2-furfurylidene malononitrile. This might possibly be related to differences in preferred rotational conformations of the side-chains.<sup>19</sup>

The signs of the side-chain couplings in the methylfurans are the same as those in methylthiophenes,<sup>2,3</sup> *i.e.*  $J_{\text{ortho}}$  negative,  $J_{\text{meta}}$  positive and  $J_{\text{para}}$  negative. The coupling  $J_{\text{CH}_3-5}$  in 2-methylfuran (-0.40 cps) is considerably larger than  $J_{\text{CH}_3-5}$  in 2-methylthiophenes.<sup>3,20,21</sup> It has been suggested<sup>3</sup> that the smallness of the coupling  $J_{\text{CH}_3-5}$  in 2-methylthiophenes is caused by a partial cancellation of a negative  $\pi$ -electron transmitted coupling and a positive  $\sigma$ -electron transmitted coupling. Evidence in support of this suggestion was obtained from a study of a substituted 2,5-dimethylthiophene in which  $J_{(\text{CH}_3)_5-(\text{CH}_3)_6}$  was found to have the value of +0.55 cps. Banwell and Sheppard<sup>18</sup> have suggested that the side-chain aldehyde couplings in aromatic aldehydes are  $\sigma$ -electron transmitted. In so far as the mechanism of the side-chain couplings to the 5-hydrogen in 2-furfurylidene malononitrile and N-(2-furfurylidene)aniline are analogous to the aldehyde coupling  $J_{\text{CHO-5}}$  in 2-furaldehydes we may consider the positive sign observed as evidence in favour of the existence of positive  $\sigma$ -electron contributions to a coupling between a side-chain  $\alpha$ -proton in a 2-substituent and the ring proton in the 5-position of a five-membered aromatic ring.

The larger magnitude of  $J_{\text{CH}_3-5}$  in 2-methylfuran as compared to 2-methylthiophene might be attributed either to a larger negative  $\pi$ -electron contribution or to a smaller (positive)  $\sigma$ -electron contribution in the furans as compared to the thiophenes. Support for one of these alternative suggestions might be obtained by a study of the coupling  $J_{(\text{CH}_3)_5-(\text{CH}_3)_6}$  in a 3-substituted 2,5-dimethylfuran.

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