Side-chain Spin Couplings in Thienothiophenes

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NMR spin coupling constants in a number of methyl and aldehyde substituted thienothiophenes have been determined. Long-range cross-ring couplings have been found in some cases. These are discussed in terms of $\sigma$-electron and $\pi$-electron contributions to the contact coupling. A comparison with the coupling constants in the corresponding unsubstituted compounds shows that the large cross-ring couplings in thieno[2,3-b]thiophene and thieno[3,2-b]thiophene are primarily transmitted through the $\sigma$-electron interaction.

Long-range interactions between protons situated on different rings in polyyring systems have been observed in a number of compounds. These couplings tend to be large between protons separated by five bonds in a zig-zag configuration. Large couplings have also been observed between protons separated by six bonds which fulfill the stereo-electronic requirement of following a straight zig-zag path.\textsuperscript{3,4} In thienothiophenes and selenothiophenes, these couplings are the largest observed.\textsuperscript{4,5} It has been proposed that residual long-range $\sigma$-induced couplings persist for the straight zig-zag paths.\textsuperscript{6}

Some insight into the nature of these couplings can be obtained by studying the side-chain couplings in methyl and aldehyde substituted compounds. The aldehyde couplings are believed to be transmitted within the $\sigma$-electron framework, and in aromatic aldehydes, they show the same stereospecific behaviour of being large only along straight zig-zag paths.\textsuperscript{7,8} Methyl couplings, on the other hand, are known to be transmitted through the $\pi$-electron framework.\textsuperscript{9,10} The theory also predicts that on the replacement of a proton directly bound to the ring system by a methyl group, the $\pi$-electron transmitted coupling should remain almost unchanged in magnitude but reverse its sign.\textsuperscript{11,12} This $C=CH \rightarrow C-C-CH_3$ replacement technique has, for instance, been used to clarify the nature of the long-range side-chain couplings in thiol-substituted thiophenes, and has been taken as evidence against a $\pi$-electron mechanism for the aldehyde couplings.\textsuperscript{13} It has also been used for a discussion of the couplings in methylated butadienes and similar compounds.\textsuperscript{14}

In the present work, we have studied the side-chain couplings in a number of methyl and aldehyde substituted thienothiophenes, where interaction across the rings might be expected.
RESULTS

2-Formyl-thieno[2,3-b]thiophene. The spectrum of 2-formyl-thieno[2,3-b]thiophene is shown in Fig. 1. The resonances from hydrogen 3 have been shifted to low field due to the electron attracting aldehyde substituent. The cross-ring coupling $J_{34} = -0.20$ Hz is very well resolved in the 4-hydrogen band. This coupling is also visible in the 3-proton band, where additional structure reveals the presence of another small coupling of magnitude 0.12 Hz.

![Diagram](image)

Fig. 1. NMR spectrum at 56.444 MHz of 2-formyl-thieno[2,3-b]thiophene in ca. 10 % acetone solution. Analysis gave the parameters (in Hz): $v_{\text{CHO}} = 552.44$, $v_3 = 459.37$, $v_4 = 419.85$, $v_5 = 432.04$, $J_{\text{CHO-3}} = +0.12$, $J_{\text{CHO-4}} = 0.00$, $J_{\text{CHO-5}} = -0.09$, $J_{34} = -0.20$, $J_{35} = 0.01$, and $J_{45} = 0.38$.

In the 5-hydrogen band, a splitting of 0.09 Hz is observed. These last-mentioned small splittings are obviously due to couplings of the 3 and 5 hydrogens to the aldehyde proton. They could, however, not be resolved in the aldehyde band. This assignment of couplings was confirmed by a double resonance experiment, in which the CHO resonance was strongly irradiated, resulting in the collapse of the 3-proton triplet and 5-proton quartet into doublets.

The signs of these small couplings cannot be determined from the spectrum, nor can a simple double resonance experiment be conceived to give these signs, since no group of three mutually coupling protons are to be found in this molecule. The sign of $J_{34}$ is assumed to be negative in agreement with unsubstituted thieno[2,3-b]thiophene.\(^4\)

3-Formyl-thieno[2,3-b]thiophene. In this spectrum, the aldehyde resonance is sharp and shows no apparent couplings to the three ring protons. The 2-proton resonance is shifted to low field, while the 4 and 5 proton resonances fall close together, forming the strongly coupled AB part of an ABMX type spectrum. In addition to the large couplings $J_{25}$ and $J_{45}$, a splitting of 0.25 Hz appears in the 2 and 4 proton bands. Analysis of the spectrum shows that this is a virtual coupling;\(^5\) the $J_{34}$ coupling in this compound is actually close to zero as in other thieno[2,3-b]thiophenes.

The assignment in this compound is based on the known magnitudes of the couplings in other thienothiophenes. The 4 and 5 proton resonances appear

\(\text{Acta Chem. Scand. 25} (1971) \text{ No. 7}\)
in reverse order compared to the unsubstituted compound, indicating a strong substituent effect of the aldehyde group into the other ring.

On irradiation of the CHO resonance by a second rf field, the 2 and 5 proton resonances remain unchanged, while the 4 proton resonance lines get sharper. This indicates the existence of a small coupling $J_{4-\text{CHO}}$, which would be a few hundredths of a Hz at most. The coupling $J_{2-\text{CHO}}$ is zero in this compound.

2-Formyl-thieno[3,2-b]thiophene. In the spectrum of 2-formyl-thieno[3,2-b]thiophene, the 6 hydrogen appears at high field as a quartet of lines, giving the large couplings $J_{56}$ and $J_{36}$, the magnitudes of which agree with the results from other thieno[3,2-b]thiophenes. The 3 proton band — shifted to low field through the influence from the CHO group — consists of two 1:2:1 triplets. The separation between the triplets gives the $J_{36}$ coupling (0.7 Hz), and the splittings between the components in the triplets are 0.12 Hz. This can only be interpreted so that the 3 hydrogen couples both to the 5 hydrogen and the CHO proton with couplings $|J_{36}| = |J_{3-\text{CHO}}| = 0.12$ Hz. However, these couplings could not be resolved in the aldehyde or the 5 hydrogen band. This indicates the presence of a cross-ring coupling over seven bonds between the CHO and 5 protons.

An attempt to estimate the magnitude of this coupling from the width of these unresolved resonance lines by calculating the line-shapes as a sum of four Lorentzian lines of width 0.12 Hz gave the result $|J_{\text{CHO}-3}| = 0.08$ Hz. Irradiation of the CHO resonance with a second rf field confirmed the existence of this coupling — the resonances in hydrogens 3 and 5 became sharper.

Although determination of the signs of the CHO couplings through selective double irradiation experiments is possible in this molecule, the small size of the splittings compared to the line-width (0.12 Hz in our spectra) made these experiments resultless. The sign of the coupling $J_{35}$ was taken as negative, as this is the case for other thieno[3,2-b]thiophenes.

3-Formyl-thieno[3,2-b]thiophene. In this compound, the CHO resonance is very narrow, and no couplings at all of the aldehyde proton to the ring protons could be found. The shifts of the proton resonances appear in the order to be expected with the hydrogen 2 resonance at low field. Analysis of the spectrum gives couplings of the same size as obtained from similar molecules.

2-Methyl-thieno[2,3-b]thiophene. In the ring-proton part of the spectrum, a 1:3:3:1 quartet with 1.2 Hz splittings appears. This indicates the presence of a coupling $J_{\text{CH}_3-3}$, the methyl coupling normally observed to protons in ortho position relative to the methyl group in substituted aromatic compounds. This coupling has been shown to be negative in methyl-substituted thiophenes. The CH$_3$ resonance appears as a doublet. No cross-ring interactions could be detected in this molecule. However, the line-width of the sample was a few tenths of a Hz, implying that not even the $J_{34}$ coupling could be resolved ($-0.15$ Hz in similar compounds). The resonance of the 3 proton appeared at higher field than the 4 and 5 protons, due to the effect of the methyl substituent.

3-Methyl-thieno[2,3-b]thiophene. The methyl resonance in this compound appears as a doublet with a splitting of 1.2 Hz. The 4 and 5 hydrogen resonances appear at low field and give the coupling $J_{35} = -1.15$ Hz, and $J_{45} = 5.21$ Hz.

in good agreement with the unsubstituted compound. The 2 hydrogen band at high field appears as a quintet due to the similar size of the two couplings $J_{25}$ and $J_{CH_2}$. No long-range couplings could be detected in this molecule.

2-Carboxy-3-methyl-thieno[2,3-b]thiophene. The CH$_3$ resonance appears as a single sharp line, and the 4 and 5 hydrogens give a simple AB pattern with $J_{45} = 5.3$ Hz. No further interactions were observed.

2,4-Dimethyl-thieno[2,3-b]thiophene. The methyl part of the spectrum consists of two doublets with almost equal splittings of 1.2 Hz, situated 12 Hz apart. The two corresponding 1:3:3:1 quartets from hydrogens 3 and 5 were only about 5 Hz apart. A double resonance experiment showed that the low field methyl group was connected to the high field proton, and the high field methyl to the low field proton. No other couplings could be found. The two 1.2 Hz couplings being practically equal, the assignment had to be based on chemical shift considerations. If we assume that the substituent effect of the two methyls are not sufficiently unequal to revert the order of the ring hydrogen bands, we can assign the 5-hydrogen to the low field band. This means that the 4 methyl group gives the high field band.

2-Carboxy-3,5-dimethyl-thieno[2,3-b]thiophene. This compound was difficult to dissolve, and the resonances from our sample were fairly weak and broad. The large coupling $J_{5CH_2} = -1.2$ Hz and the shifts of the resonances could be determined.

![Image of NMR spectrum](image)

**Fig. 2.** NMR spectrum at 56.44 MHz of 2-methyl-thieno[3,2-b]thiophene in ca. 20% CCl$_4$ solution. The analysis finally gave the parameters (in Hz): $v_{CH} = 139.29$, $v_5 = 382.85$, $v_s = 401.31$, $v_4 = 396.75$, $J_{CH_2} = -1.18$, $J_{CH_2} = -0.35$, $J_{CH_2} = 0.08$, $J_{45} = -0.16$, $J_{45} = 0.69$, $J_{45} = 5.24$.

2-Methyl-thieno[3,2-b]thiophene. The ABCX$_3$ spectrum of 2-methyl-thieno-[3,2-b]thiophene is reproduced in Fig. 2. The assignment can, as in the other compounds studied, be based on the magnitudes of the observed ring coupling constants. This agrees with the chemical shifts — the proton ortho relative to the methyl group is shifted to higher field. The usual coupling between the methyl group and the ortho proton (-1.2 Hz) is readily recognized. The cross-ring coupling across five bonds $J_{35} = 0.7$ Hz is recognized from other thieno-[3,2-b]thiophenes. However, an additional cross-ring interaction between the methyl protons and hydrogen 5 can be observed, this coupling being $|J_{5CH_2}| = 0.35$ Hz.

The sign of this coupling cannot be determined by selective double resonance experiments, as the small interaction $J_{38}$ completely disappeared in this spectrum. Nor can any coupling be found between the CH$_3$ group and hydrogen 6. The sign of the coupling $J_{\text{CH}-5}$ can, however, be determined by a general double resonance experiment.

The method employed here consists of placing a strong non-selective H$_2$ field somewhere in the ABC part of the spectrum, while the methyl resonance is observed. For certain values of H$_2$ and $v_2$, the methyl quartet can be expected to show some type of asymmetry. The same type of experiment has been performed by Forsén et al. on ABX and ABCX$_3$ spin systems.$^{17,18}$

The general double resonance Hamiltonian for the ABCX$_3$ system gives a $64 \times 64$ matrix. A first step towards simplification is to treat the spectrum as a superposition of two identical ABCX spectra and one ABCQ spectrum, where Q stands for a spin $3/2$. The double resonance Hamiltonian for an ABCD system is given in Ref. 18, and this matrix can also be used for the ABCX$_3$ system under consideration, if we make the following modifications. The ABCX double resonance Hamiltonian can be obtained from the ABCD Hamiltonian in Ref. 18 by neglect of the off-diagonal elements containing the X coupling constants, and neglecting the effect of the irradiating H$_2$ field on the X part of the spectrum. The ABCQ Hamiltonian can be obtained from the ABCX Hamiltonian if it is realized that the ABC part in an ABCX spectrum can be looked upon as a superposition of two ABC spectra with different "effective chemical shifts" due to the couplings to the X group, the X group having magnetic quantum number $m_X = \pm 1/2$. Thus the ABCX matrix is obtained from the ABCX matrix by simply replacing $m_X \rightarrow m_Q = \pm 3/2$, $\pm 1/2$.

These simplifications will result in 4 different $8 \times 8$ matrices for the ABC part, corresponding to $m_X = m_Q = \pm 1/2$, and $m_Q = \pm 3/2$. These $8 \times 8$ matrices were diagonalized numerically, and the X transitions calculated as transitions between different matrices. The calculated intensities for the transitions between matrices for spin $\pm 1/2$ were multiplied by a factor of three (two from ABCX and one from ABCQ). A Lorentzian line shape function was assumed for all these X transitions. By finally adding all these contributions, a theoretical spectrum of the methyl part could be obtained for any choice of amplitude and frequency of the H$_2$ field.

After having determined a suitable amplitude for H$_2$, a number of experimental observations were made for different $v_2$ offsets in the ABC part of the spectrum. These spectra were run on an extra recorder where they were broadened by a factor of ten, making the asymmetries more apparent. Theoretical curves were calculated for the same $v_2$ offsets. The sign of the $J_{\text{CH}-3}$ coupling constant was taken as negative, in accordance with all other experimental results, and the calculations were carried out for the two possible signs of the unknown coupling constant $J_{\text{CH}-5}$. The experimental and theoretical double resonance curves are shown in Fig. 3. It is seen that a satisfactory fit of experimental and theoretical spectra is only obtained if $J_{\text{CH}-5}$ is assumed to be negative, i.e. $J_{\text{CH}-5} = -0.35$ Hz.

A complete analysis of the spectrum was now possible, using a least squares fit of experimental and theoretical spectra. The proton-proton coupling $J_{35}$

was found to be $-0.16$ Hz, a value which is in good agreement with other thieno(3,2-b)thiophenes. The analysis also gave the coupling $J_{\text{CH}_3}$ as being non-zero ($0.08$ Hz).

3-Methyl-thieno[3,2-b]thiophene. The spectrum of this compound is shown in Fig. 4. The assignment is easily made, noting the large cross-ring coupling

$$\text{Fig. 3. Double resonance spectra of the methyl group in 2-methylthieno[3,2-b]thiophene. The upper part of the figure shows computer calculated spectra with } J_{\text{CH}_3}= +0.35 \text{ Hz, the middle part the actually recorded spectra, and the lower part the computer calculated spectra with } J_{\text{CH}_3}= -0.35 \text{ Hz. The irradiation amplitude was } 5.75 \text{ Hz, and the } v_4 \text{ frequencies } 392.14, 394.85, \text{ and } 398.00 \text{ Hz from TMS.}$$

$$\text{Fig. 4. NMR spectrum at } 56.444 \text{ MHz of 3-methyl-thieno[3,2-b]thiophene in ca. } 20 \% \text{ acetone solution. Analysis gave the parameters (in Hz) } v_3 = 360.61, v_{\text{CH}_3} = 130.10, v_4 = 419.96, v_5 = 410.72, J_{\text{CH}_3} = -1.17, J_{\text{H}_3} = 1.98, J_{\text{H}_3} = 0.10, J_{\text{CH}_3} = 0.00, J_{\text{CH}_3} = 0.00, \text{ and } J_{\text{H}_3} = 5.21. \text{ The coupling } J_{\text{CH}_3} \text{ is, however, not quite zero, as is seen from the result on the 5 proton band, when the high-field CH}_3^\beta \text{ line is irradiated by a second rf field.}$$

(A part of the double resonance spectrum is inserted in the figure.)

$J_{26} = 1.5$ Hz found in these molecules. The small coupling $J_{26}$ cannot be resolved; the analysis, however, gives the value $J_{26} = -0.10$ Hz. The result of a double resonance experiment, in which the high-field methyl resonance line was irradiated, is inserted in Fig. 4. The hydrogen 6 band remains unchanged, while the first and the third line in the hydrogen 5 band get more narrow and appear higher. The effect is small, but it shows the existence of a small interaction $J_{\text{CH}-5}$. This also confirms the different signs of $J_{\text{CH}-2}$ and $J_{25}$. A complete analysis of the spectrum results in a zero value for the coupling $J_{\text{CH}-5}$.

2-Carboxy-3-methyl-thieno[3,2-b]thiophene. The resonance lines in the spectrum of this compound were fairly broad, consisting of one line from the methyl group and a simple AB pattern from the ring hydrogens. All lines were of the same width, and even though irradiation of the methyl resonance seemed to make the AB transitions more narrow, no certain conclusions could be drawn from this effect.

2,6-Dimethyl-thieno[3,2-b]thiophene. In the spectrum of this compound, both ring hydrogens have almost identical chemical shifts, the 3 proton band consisting of 4 strong peaks, while the 5 proton band owing to couplings to both methyl groups consists of 16 lines. The 6-methyl group gives a doublet with the usual spacing of 1.2 Hz, while the 2-methyl group gives rise to a quartet. A long-range coupling $J_{2\text{CH}-5}$ of about 0.3 Hz could also be resolved. No methyl-methyl coupling could be seen in the spectrum. The sign of $J_{2\text{CH}-5}$ was determined by a selective double resonance experiment, in which the 2-methyl resonances were irradiated and collapses in the 6-methyl quartet studied. Small but significant asymmetries appeared, and $J_{2\text{CH}-5}$ was found to be of the same sign as $J_{3\text{CH}-5}$, i.e. negative, which is in accordance with the result obtained in 2-methyl-thieno[3,2-b]thiophene.

2-Carboxy-3,5-dimethyl-thieno[3,2-b]thiophene. This compound was difficult to dissolve. The two methyl groups have practically identical chemical shifts, and the only coupling obtained from the spectrum was $J_{5\text{CH}-6}$. No methyl–methyl interaction could be observed.

**DISCUSSION**

The largest cross-ring couplings in unsubstituted thienothiophenes have been observed between protons separated by six bonds in a straight zig-zag configuration, i.e. $J_{26} = 1.5$ Hz in thieno[3,2-b]thiophene, and $J_{26} = 1.2$ Hz in thieno[2,3-b]thiophene. When the 2 hydrogen is replaced by an aldehyde group, a small coupling $J_{\text{CHO}-5}$ can still be observed, this coupling being reduced below 0.1 Hz. Such a reduction of the coupling can be expected with the increasing number of bonds if a $\sigma$-electron interaction is assumed for the contact coupling.

The aldehyde couplings have been shown to be stereospecific, being large only along straight zig-zag paths. In the 2-substituted thienothiophenes, one of the rotational conformations gives a straight zig-zag configuration for the coupling to the 5 proton of the kind which has been found favourable for long-range aldehyde couplings in other aromatic compounds, e.g. benzenes. These couplings have been observed to be large over five bonds. In the thieno-

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thiophenes, this coupling has to be transmitted over seven bonds, and substantial reduction of the magnitude of this coupling is not unexpected.

The ortho couplings in the aldehyde substituted thienothiophenes seem to exist only when the CHO group is in a position relative to S. These couplings have not been reported in thiophenes before. The sign of this small coupling (0.12 Hz) was not determined in this study, but in analogy with CHO-substituted benzenes it could be assumed to be negative. The sign of this coupling in fluorothiophenes has been determined by Rodmar et al. 21

A methyl group in the 2 position of thieno[2,3-b]thiophene does not couple to protons on the other ring, not even to the 5-position hydrogen, which shows the largest long-range coupling in the unsubstituted compound, \( J_{25} = 1.20 \) Hz. This would indicate that the cross-ring coupling \( J_{25} \) is not a \( \pi \)-electron transmitted contact coupling according to the criterion of Hoffman and Gronowitz of approximately constant magnitude and sign reversal of a \( \pi \)-electron coupling on methyl substitution.

In 2-methyl-thieno[3,2-b]thiophene and in 2,6-dimethylthieno[3,2-b]thiophene, on the other hand, the methyl group couples to the 5 proton with a coupling constant \( J_{CH-5} \approx -0.35 \) Hz. The finite magnitude and the reversed sign to the coupling in the unsubstituted compound \( J_{25} \approx 1.5 \) Hz, strongly indicates that this coupling is partially \( \pi \)-electron transmitted.

The \( J_{CH-6} \) couplings in the methyl substituted thieno[3,2-b]thiophenes turned out to be zero. In the unsubstituted compound, this coupling is \( J_{36} = 0.75 \) Hz, and if one uses the same line of reasoning, this coupling appears not to be \( \pi \)-electron transmitted.

The theoretical expression for the magnitude of the \( \pi \)-electron contribution to the couplings in unsaturated compounds, as calculated by Karplus, has recently been modified, leading to a substantial reduction of \( \pi \)-electron transmitted couplings and also indicating that the \( \sigma \)-contribution could be of importance also over five bonds. 22 This work is restricted to acyclic unsaturated compounds, however, as are also the works by several authors who have discussed the long-range couplings in butadienes, using different approaches. 23-25

Our results in this investigation indicate that the cross-ring couplings in thienothiophenes are primarily transmitted by some other mechanism than a \( \pi \)-electron contact coupling (with the possible exception for the \( J_{25} \) coupling in thieno[3,2-b]thiophene). The results of this study are in agreement with the suggestion of Banwell and Sheppard 8 of a residual \( \sigma \)-induced long-range coupling which persists for straight zig-zag paths.

**EXPERIMENTAL**

The compounds used in this investigation were prepared according to Ref. 26. The solvent employed was acetone (exceptions noted in Table 1), and the concentration in the samples were 15–20 % by weight, with exception for the carboxy substituted compounds which had a concentration of only a few percent. All spectra were run on a Varian HA-60 spectrometer operating at 56.444 MHz, with TMS serving as lock signal and reference. A Muirhead D-890-A oscillator was employed in the double resonance experiments.

Table 1. Chemical shifts and coupling constants (in Hz) in some substituted thienothiophenes.

**Thieno[2,3-b]thiophenes**

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<th>Substituent</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$v_4$</th>
<th>$v_5$</th>
<th>$J_{23}$</th>
<th>$J_{24}$</th>
<th>$J_{25}$</th>
<th>$J_{26}$</th>
<th>$J_{27}$</th>
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<td>CHO (2)</td>
<td>552.4</td>
<td>459.4</td>
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<td>408.2</td>
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**Thieno[3,2-b]thiophenes**

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<th>Substituent</th>
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<th>$v_5$</th>
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<td>—</td>
<td>0.0</td>
<td>5.22</td>
</tr>
<tr>
<td>CH$_3$ (2), CH$_3$ (6)</td>
<td>140.5</td>
<td>388.1</td>
<td>390.1</td>
<td>128.4</td>
<td>-1.19</td>
<td>-0.32</td>
<td>0.00$^e$</td>
<td>0.00</td>
<td>0.00</td>
<td>-1.15</td>
</tr>
<tr>
<td>CH$_3$ (3), CH$_3$ (5), COOH (2)$^f$</td>
<td>146.9</td>
<td>146.7</td>
<td>406.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.0</td>
<td>0.0</td>
<td>-1.17</td>
</tr>
<tr>
<td>Unsubstituted (Ref. 4)</td>
<td>421.9</td>
<td>411.8</td>
<td>421.9</td>
<td>411.8</td>
<td>5.25</td>
<td>1.55</td>
<td>-0.20</td>
<td>-0.20</td>
<td>0.75</td>
<td>5.25</td>
</tr>
</tbody>
</table>

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$^a$ The shifts are given at 56.444 MHz, relative to TMS as internal reference.

$^b$ Sign unknown.

$^c$ Experimentally shown non-zero.

$^d$ Estimated from line-widths.

$^e$ Solvent CCl$_4$.

$^f$ Solvent dimethylformamide.
Acknowledgements. The authors wish to thank Professor Kai Siegbahn for all facilities placed at their disposal. Thanks are also expressed to Malmfonden, Swedish Foundation for Scientific Research, and to the Swedish Natural Science Research Council, for providing the funds necessary to purchase the spectrometer.

REFERENCES


Received December 22, 1970.