Long-range Proton-proton Spin Coupling Constants in Selenothiophenes

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The cross-ring coupling constants in seleno[2,3-b]thiophene and seleno[3,2-b]thiophene, as well as their 5-carboxy substituted derivatives have been determined. The largest couplings are observed between protons separated by six bonds placed in a straight zig-zag path, this coupling being 1.5 Hz in seleno[3,2-b]thiophene and 1.1 Hz in seleno[2,3-b]thiophene. The coupling *via* five bonds in seleno-[3,2-b]thiophene is 0.7 Hz. The remaining couplings are small. The results are compared with those obtained in the corresponding thienophenes. Couplings between [77]Se and the selenophene ring protons are observed and determined to be of the same sign.

The proton magnetic resonance spectra of the five-membered heteroaromatic systems thiophene and furan have been thoroughly studied, and the magnitudes of the proton spin coupling constants are well known in these molecules, including their dependence on substituents.[1,2] This study of the NMR parameters of the group VI heterocycles has been extended to include a few selenophenes.[3,4] The close similarity of the spin coupling constants and chemical shifts in thiophene and selenophene have been taken as an indicator of the close resemblance of the molecular structure of these two heterocycles.

In a recent study we have investigated the long-range cross-ring coupling constants in thienothiophenes, and found these couplings to be largest between protons situated in a straight zig-zag configuration.[5] The present communication presents the results of an extension of this study to selenothiophenes, where similar long-range interactions might be anticipated.

RESULTS

5-Carboxyseleno[2,3-b]thiophene. This compound gives an ABX type spectrum, where the X band can be assigned to the proton in the selenophene part of the molecule. In the AB part of the spectrum the upfield B-band is assigned to hydrogen 3 in analogy with the assignment in thiophene itself

and the thienothiophenes.[1,5] The AB coupling constant $J_{AB} = J_{23} = 5.18$ Hz is similar to the corresponding coupling in thiophene and thieno[2,3-b]thiophene. A coupling $|J_{BX}| = |J_{34}| = 0.18$ Hz could be resolved, but no coupling $J_{AX} = J_{24}$ was observed. This is in accord with results from thieno[2,3-b]thiophene where a coupling constant $J_{34} = -0.18$ Hz was observed, while J_{24} was negligible. The sign of J_{34} could not be determined in the present case, but it is most likely the same as in thieno [2,3-b]thiophene, i.e. $J_{34} = -0.18$ Hz.

Seleno[2,3-b]thiophene. The ABCD spectrum of seleno[2,3-b]thiophene is depicted in Fig. 1. The spectrum is seen to be sufficiently loosely coupled to
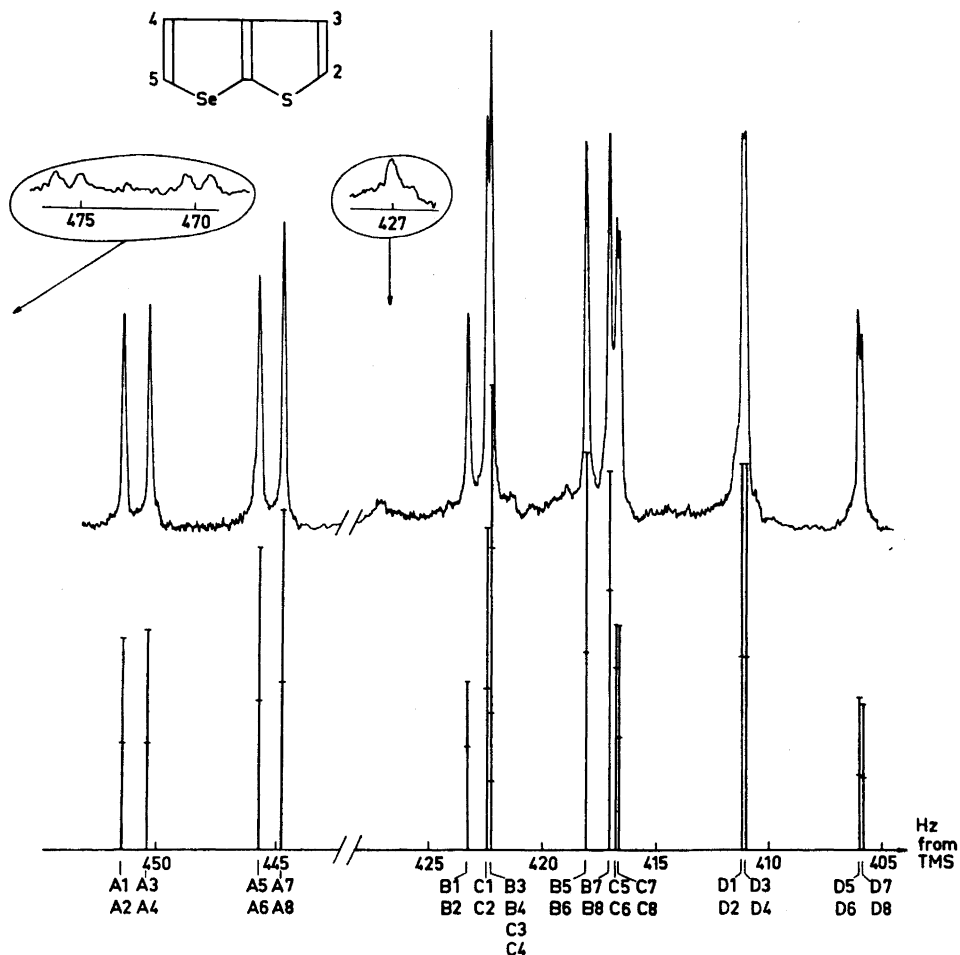

Fig. 1. The NMR spectrum at 56.444 MHz of seleno[2,3-b]thiophene in *ca.* 10 % acetone solution. The [77]Se satellites, recorded with a higher gain, are included in the figure. The theoretical spectrum is calculated with the parameters given in Table 1.

render possible a first order assignment of transitions as indicated in the figure. The B and D bands are assigned to the protons in the thiophene part of the molecule. This assignment is based on the size of the J_{BD} coupling (5.2 Hz) which is similar to that in the 5-carboxyseleno[2,3-b]thiophene, and other thienothiophenes. The J_{AC} coupling (5.7 Hz) is larger in agreement with observations that selenophene couplings are larger than the corresponding thiophene couplings.[3,4] The resonances in selenophenes have been observed to occur at lower field than in the corresponding thiophenes, this stronger shielding in thiophenes being attributed to a more effective lone-pair conjugation of S than of Se.[4] This is in accord with the discussed assignment in seleno-[2,3-b]thiophene.

A least squares fit of observed and theoretical transition frequencies, based on an exact ABCD treatment, gives the following coupling constants (in Hz) $J_{23} = 5.22$, $J_{24} = 0.00$, $J_{25} = 1.12$, $J_{34} = -0.17$, $J_{35} = -0.06$, $J_{45} = 5.66$. The small value of J_{35} is regarded as rather uncertain since the coupling is not directly discernible as a splitting in the spectrum. A least squares fit where this coupling is set equal to zero, gives a root-mean square deviation of 0.03 Hz to be compared with that of 0.01 Hz obtained with freely varying parameters. The signs of J_{34} or J_{25} cannot be obtained from the spectrum, nor can a simple double resonance experiment be devised to give these signs, since we do not have a group of three nuclei in the molecule which all couple to each other. The signs given are based on the analogy with the thieno[2,3-b]thiophene. The theoretical spectrum is included in Fig. 1.

Couplings between the ^{77}Se isotope of spin $\frac{1}{2}$ and the ring protons in the selenophene ring is revealed by the presence of satellites on the low field side of the 4 and 5 hydrogen bands, separated from the main resonance by 24.6 Hz and 4.7 Hz, respectively. The satellites are shown in Fig. 1. The relative signs of the two $J_{^{77}Se-H}$ couplings were determined by a decoupling experiment in which the 5-proton low field satellites were irradiated by a strong decoupling rf field. This led to the collapse of the low field satellite band of the 4 hydrogen, i.e. to the disappearance of the satellite doublet shown in Fig. 1 which will now fall below the main resonance. This shows that the two $^{77}Se - H$ couplings are of the same sign. The couplings are $J_{^{77}Se-5} = \pm 49.2$ Hz and $J_{^{77}Se-4} = \pm 9.4$ Hz, their absolute sign being undetermined.

5-Carboxyseleno[3,2-b]thiophene. The spectrum of this compound appears as an ABX spectrum, where the X-band can be assigned to the proton in the selenophene part of the molecule. The X-band consists of a doublet of splitting 0.65 Hz, also apparent in the B-band revealing a coupling of this magnitude between the 6 and 3 protons. A complete analysis gives the coupling constants (in Hz) $J_{23} = 5.25$, $J_{26} = -0.02$ and $J_{36} = 0.67$. The sign of J_{36} relative to J_{23} cannot be obtained from the spectrum, it has been chosen to agree with results from thieno[3,2-b]thiophene and results discussed below.

Seleno[3,2-b]thiophene. The ABCD spectrum of seleno[3,2-b]thiophene is depicted in Fig. 2. Although the spectrum is strongly coupled, the large *ortho* couplings in the two rings can be recognized providing a basis for the assignment. The A,B part is thus assigned to the selenophene protons while the C,D band is assigned to the thiophene part of the molecule, the arguments being the same as for the isomer seleno[2,3-b]thiophene.
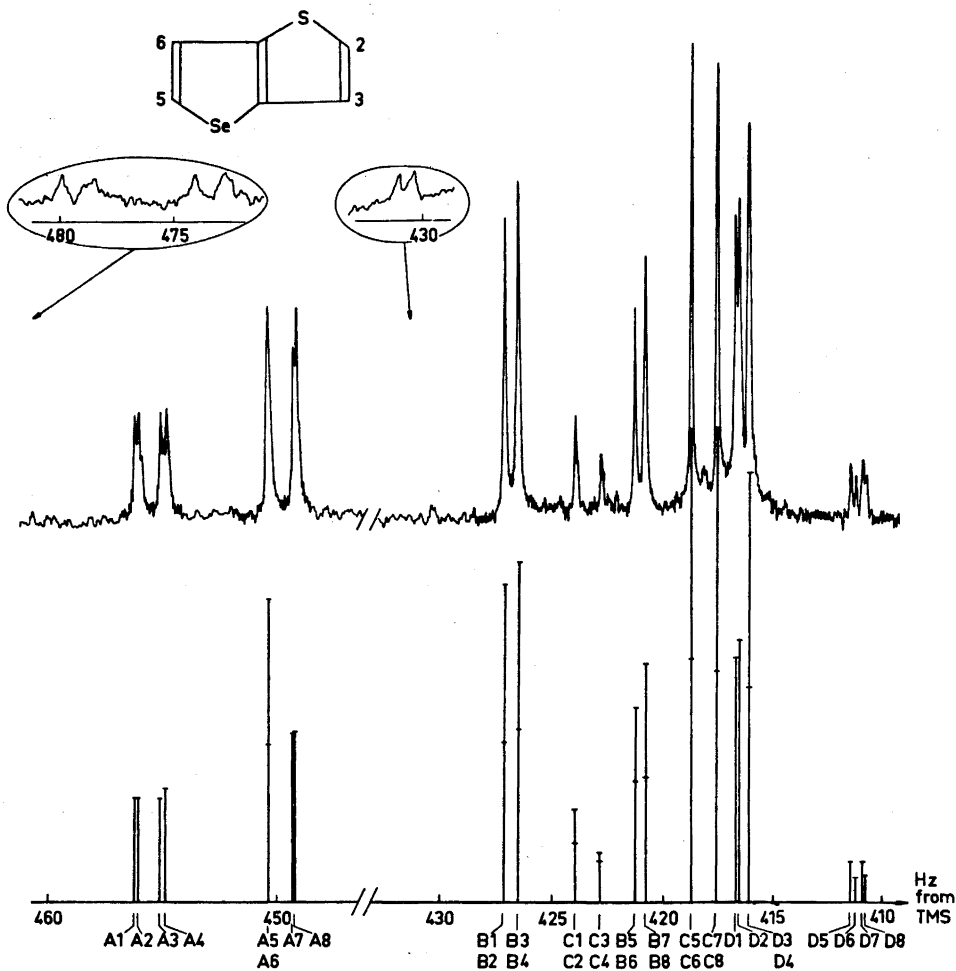
Fig. 2. The NMR spectrum at 56.444 MHz of seleno[3,2-b]thiophene in *ca.* 18 % acetone solution. The ^{77}Se satellites, recorded with a higher gain, are included in the figure. The theoretical spectrum is calculated with the parameters given in Table 1.

Before a complete computer analysis was attempted, the relative signs of a number of couplings were determined by double irradiation experiments. In discussing these experiments, for simplicity the first order nomenclature will be employed, although due to the strong coupling of the spectrum, line separations and coupling constants are no longer equivalent.

Inspection of the spectrum shows the presence of a small coupling between the A and D protons. Since the products $J_{AB} \cdot J_{BD}$ and $J_{AC} \cdot J_{CD}$ are both different from zero a decoupling of J_{AD} would give the relative signs of these

two pairs of coupling constants.[6] The strong coupling of the spectrum has already produced a collapse of lines of the kind we want to produce in a selective decoupling experiment. The A5,A6 doublet is collapsed as is also the D3,D4 doublet, indicating that J_{AB} and J_{BD} are of equal sign, as are also J_{AC} and J_{CD}. This interpretation is also confirmed by a selective double irradiation experiment in which irradiation of the D1,D2 doublet leads to the collapse of the A1,A2 doublet. Similarly irradiation of the D7,D8 doublet leads to a collapse of the A7,A8 doublet.

The employment of similarities in double irradiated spectra and strongly coupled single resonance spectra for the determination of relative signs of spin coupling constants has first been discussed by Freeman et al.[7,8]

If we continue to use the first order terminology and set the splittings equal to the coupling constants, it would now appear tempting to determine the sign of the small coupling J_{AD} relative to J_{AB} by decoupling of J_{BD}. The results of this experiment are depicted in Fig. 3. Irradiation of the B1 − B4
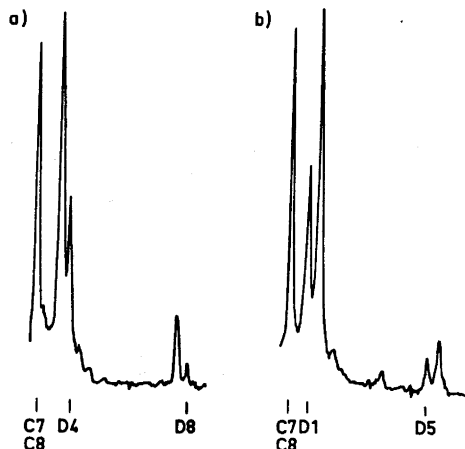

Fig. 3. Results of the double irradiation experiment in seleno[3,2-b]thiophene. The figure shows the D band of the spectrum, when the perturbing rf field H_2 is centred on a) the B1 − B4 lines b) the B5 − B8 lines.

multiplet leads to the collapse of the line pairs D1,D3 and D5,D7, while irradiation of the B5 − B8 multiplet collapses lines D2,D4 and D6,D8. In first order terms this would indicate that J_{AD} is positive. What has been established by the experiment, however, is that transitions B1,B2 and D1,D3 are connected to form a closed polygon in the energy level diagram as do also B2,B4 and D5,D7, etc.[6]

When this assignment of transitions is fed into a computer for a complete ABCD analysis, the computer gives J_{AD} as negative. The strong coupling of the C and D protons together with a sufficiently large J_{AC} coupling has thus led to a reversal of the order of transitions from what should be anticipated on a first order basis, amply illustrating the danger of identifying coupling constants with splittings in a strongly coupled spectrum.

A least squares fit of observed and theoretical transition frequencies gives the coupling constants (in Hz) $J_{23} = 5.21$, $J_{25} = 1.49$ $J_{26} = -0.17$, $J_{35} = -0.16$,

$J_{36} = 0.72$, and $J_{56} = 5.75$. The complete analysis gives a negative coupling constant $J_{BC} = J_{26} = -0.17$ Hz, a coupling which is not directly observable as a splitting in the spectrum. Since the spectrum is very well resolved and the B and C lines are sharp, the value of J_{BC} given by the computer is well founded. This value of J_{BC} also agrees with the corresponding crossring coupling *via* the selenium atom, J_{26} and also with the corresponding cross ring coupling in thieno[3,2-b]thiophene.

The satellites due to the couplings of the selenophene ring protons to the ^{77}Se nucleus are well resolved also in this compound. They are included in Fig. 2. The two couplings were found to be of equal sign by a decoupling experiment entirely analogous to that described for seleno[2,3-b]thiophene. The couplings are $J_{^{77}Se-5} = \pm 47.6$ Hz and $J_{^{77}Se-4} = \pm 7.8$ Hz.

DISCUSSION

The spin coupling constants and chemical shifts observed in the seleno-thiophenes are summarized in Table 1. For comparison the coupling constants in the corresponding thienothiophenes are included in the table.

The cross-ring coupling constants in the selenothiophenes show the same pattern as in the thienothiophenes, being large only between protons situated in a straight zig-zag configuration. The zig-zag rule has previously been observed in a number of poly-ring systems involving the heteroatoms S, N, and O (see Ref. 9 and references given there).

The selenothiophene cross-ring couplings do not only show the same general patterns as those in the thienothiophenes, but the two sets of coupling constants are equal to within a few hundredths of a Hz, even in the couplings transmitted via six bonds. This would indicate a close similarity in the electronic structure and the geometrical shape of the selenothiophenes and the corresponding thienothiophenes.

EXPERIMENTAL

5-Carboxyseleno[2,3-b]thiophene and seleno[2,3-b]thiophene were prepared as described in Ref. 10. The isomeric seleno[3,2-b]thiophenes have been described previously be Goldfarb.[11] The syntheses were accomplished by adopting the methods of Goldfarb *et al.*[12] and Bugge [13] for the preparation of the thieno[3,2-b]thiophenes. The introduction of selenium was, however, carried out with tetrahydrofuran as a solvent.

The NMR spectra were obtained using a Varian HA-60 spectrometer operating at 56.444 MHZ. All spectra were recorded in the frequency sweep mode; TMS served as lock signal for the internal stabilization. In the decoupling experiments the second rf field was obtained by amplitude modulation of the magnetic field. The modulation frequency was produced by a Philips oscillator PP 6050.

Table 1. Chemical shifts ^{a} and coupling constants in selenothiophenes and thienothiophenes.

	ν_2	ν_3	ν_4	ν_5	J_{23}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}	J_{Se-4}	J_{Se-5}
Seleno[2,3-b]thiophene ^{b}	419.55	409.13	419.79	447.81	5.22	0.00	1.12 *	−0.17 *	−0.06	5.66	± 9.4	±49.2
5-Carboxyseleno[2,3-b]-thiophene ^{c}	430.85		463.29		5.18	0.0	—	−0.18 *	—	—		
Thieno[2,3-b]thiophene		418.49			5.23	−0.02	1.20	−0.18	−0.02	5.23		

	ν_2	ν_3	ν_5	ν_4	J_{23}	J_{25}	J_{26}	J_{35}	J_{36}	J_{56}	J_{Se-5}	J_{Se-6}
Seleno[3,2-b]thiophene ^{d}	419.59	414.93	452.42	424.27	5.21	1.49	−0.17	−0.16	0.72	5.75	±47.6	± 7.8
5-Carboxyseleno[3,2-b]-thiophene ^{e}	436.93	422.63			5.25		−0.02		0.66			
Thieno[3,2-b]thiophene			467.81		5.25	1.55	−0.20	−0.20	0.75	5.25		

^{a} The shifts are given at 56.444 MHz relative to TMS as internal reference. The uncertainty in the parameters are estimated to be generally less than 0.04 Hz, except for the selenium couplings which have an uncertainty of ±0.2 Hz. ^{b} Ca. 10 % in acetone. ^{c} Ca. 5 % in acetone. ^{d} Ca. 18 % in acetone. ^{e} Ca. 8 % in acetone. ^{f} Ca. 8 % in acetone. * Sign based on analogy with thieno[2,3-b]thiophene.

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