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DETERMINATION OF THE SIGNS OF SELENIUM-PROTON COUPLING CONSTANTS IN SOME 2,4-DISUBSTITUTED SELENOPHENES

M.P. SIMONNIN[x], M.J. POUET[x] et C. PAULMIER[xx]

[x]Laboratoire de Spectrographie de l'E.N.S.C.P.
Equipe de Recherche associée au C.N.R.S. N° 390
11, rue Pierre et Marie Curie, 75005 - PARIS

[xx]Laboratoire de Chimie Organique, Faculté des Sciences de Rouen, 76130 - MONT-ST-AIGNAN

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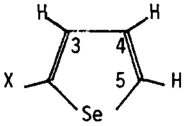
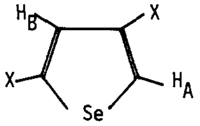
A recent study of the ^{77}Se NMR spectra of some 2-substituted selenophenes (1) has shown that the three Se-H coupling constants fall in defined regions : $|J_{Se-H_5}| >> |J_{Se-H_4}| > |J_{Se-H_3}$ Moreover, for the 2-haloselenophenes, these coupling constants are dependent with the Pauling's electronegativity values : $|J_{Se-H_5}|$ increases with the halogen electronegativity while $|J_{Se-H_3}|$ and $|J_{Se-H_4}|$ decrease when the halogen becomes more electronegative.

A few Se-H coupling constants have been determined in some cyclic derivatives of selenium(2-4) but the signs of these coupling constants have not been reported.

We describe here our first results concerning the determination of the signs of J_{Se-H} in 2,4-disubstituted selenophenes : Homo and Heteronuclear Double Resonance experiments (5) show $^2J_{Se-H}$ to be positive and $^3J_{Se-H}$ to be positive or negative.





X = Br, CN, NO_2

The relative signs of $^2J_{Se-H}$ and $^3J_{Se-H}$ were determined by homonuclear double resonance experiments performed by irradiating ^1H at 100 MHz and observing the proton satellites due to molecules containing the ^{77}Se isotope - Tickling or selective decoupling indicate that these coupling constants are of the same sign in the dibromo and dicyano derivatives, but are of opposite sign in the dinitro compound.

Heteronuclear Tickling experiments were performed in order to get the relative signs of $^3J_{Se-H}$ and $^4J_{H-H}$: irradiation of ^{77}Se at 19.09 MHz indicates that these coupling constants are of the same sign in the dibromo and dicyano selenophenes but are of opposite sign in the dinitro derivative.

Finally the relative signs of $^3J_{H-H}$ and $^4J_{H-H}$ were determined by homonuclear INDOR experiments, performed on the main proton spectrum of 2-bromoselenophene. The results prove the three coupling constants $J_{H_3-H_4}$, $J_{H_3-H_5}$, $J_{H_4-H_5}$ to be of the same sign, hence positive.

These results, collected in Table 1, allow us to conclude that $^2J_{Se-H}$ is positive in the three 2,4-disubstituted selenophenes examined, while $^3J_{Se-H}$ is positive in the dibromo and dicyano derivatives but negative in the 2,4-dinitroselenophene. The change in sign of $^3J_{Se-H}$ observed in this last case seems to be due to the influence of two electron-attracting substituents in the ring : this conclusion is in agreement with the influence of electronegativity on $^3J_{Se-H}$ described by Gronowitz and coworkers (1). A study of other substituted selenophenes is in progress in order to confirm this preliminary interpretation.

Table 1

NMR Parameters of 2,4-disubstituted Selenophenes(a) (Solvent : DMSO-d_6)

Substituent X	δ_A	δ_B	$^4J_{H_A-H_B}$	$^2J_{Se-H_A}$	$^3J_{Se-H_B}$
Br	8.17	7.41	+ 1.7	+ 42.5	+ 3.5
CN	9.55	8.55	+ 1.4	+ 40.7	+ 2.1_8
NO_2	9.51	8.72	+ 2.1_7	+ 37.7	- 0.4 (b)

(a) Varian XL-100-12-W.G. (TMS, internal reference)

(b) Value deduced from homo and heteronuclear Tickling experiments

The $^2J_{Se-H}$ coupling constants given in Table 1 are greater than the corresponding values reported for dialkylselenium : + 10.5 in dimethylselenium (6) and + 10.6 in diethylselenium (7).

So, a change in the hybridization of the carbon and the cyclic structure make $^2J_{Se-H}$ more positive. This augmentation seems to be due to the increase of the s character of the carbon atom orbital bonding to selenium, as pointed out by Manatt and coworkers for P-H coupling constants (8).

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