Nuclear Magnetic Resonance of Aromatic Heterocyclics. VIII. A Comparative Study of ^{1}H and ^{13}C Spectra of Some 2-Substituted Furans, Thiophenes, Selenophenes and Tellurophenes

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A systematic investigation of the influence of the heteroatom on ^{1}H- and ^{13}C-NMR parameters in 2-substituted furans, thiophenes, selenophenes and tellurophenes has been carried out. In addition to the parent compounds, the formyl, acetyl, carboxyl, carbomethoxy, methylthio and hydroxymethyl derivatives were studied.

Linear correlations between the electronegativity of the heteroatoms and several of the NMR parameters were observed, as well as between the shifts of the corresponding protons and carbons in the four heterocyclic series. These can be used for predicting shifts of unknown selenophene and tellurophene derivatives, when those of thiophene are known.

^{125}Te $-$ H couplings were determined for the tellurophenes and compared with ^{77}Se $-$ H couplings.

Extensive work on the effect of substituents on the proton NMR parameters of thiophenes,[1,2] furans,[3] and selenophenes [4] have previously been carried out by Gronowitz and coworkers. As early as 1962 a linear correlation between the 3-proton shifts in 2-substituted thiophenes and the corresponding shifts in 2-substituted furans was observed. The same was also found for the 5-proton shifts. We were therefore interested in extending this investigation to the selenophene and tellurophene series, as well as in extending our study to ^{13}C NMR. Only a few ^{13}C NMR investigations of these heterocyclic systems have been carried out,[5–9] from which basic information about chemical shift regions and most ^{13}C $-$ H couplings may be obtained.

Takahashi and coworkers,[9] who studied six 2- and six 3-substituted thiophenes, observed a linear correlation between the C_2 shift of 3-substituted derivatives and the C_3 shift in 2-substituted compounds, and also a linear correlation between C_5 shifts and H_5 shifts of 2-substituted thiophenes.

A systematic study of the influence of the heteroatom of these four related aromatic systems on the transmittance of substituent effects to different positions of the rings would perhaps provide some information related to the aromaticity of these rings and could contribute to an understanding of the chemical differences between these systems. Both experimental results and theoretical calculations have indicated that correlations exist between ^{13}C chemical shifts and charge densities.

In the present paper, due to synthetic difficulties in preparing 2-substituted tellurophenes, the series of derivatives studied had to be limited to the 2-formyl, 2-acetyl, 2-carboxyl, 2-carbomethoxy, 2-hydroxymethyl, and 2-methylthio derivatives of furan, thiophene, selenophene, and tellurophene, besides the parent compounds. This number and types of substituents are of course not representative enough for a test of the applicability of the Swain and Lupton two-parameter equation, which hitherto has been successfully applied by us to the chemical shifts of 5- and 4-substituted 2-fluorothiophenes and 5-substituted 3-fluorothiophenes,[10,11] as well as to proton chemical shifts of thiophenes [1,2] and selenophenes.[4]

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Table 1. ^{1}H NMR data for some furan, thiophene, selenophene, and tellurophene derivatives in deuterioacetone solution at 100 MHz using TMS as internal standard. X = heteroatom and r = correlation coefficient for correlation with electronegativity.

Substituent	X	δ_3	δ_4	δ_5	δ_{HX}	J_{34}	J_{35}	J_{45}
	O	7.45	6.74	7.94	7.72	3.45	0.83	1.73
	S	7.93	7.30	7.96	9.98	3.79	1.22	4.75
CHO	Se	8.17	7.54	8.68	9.86	3.90	1.22	5.44
	Te	8.62	8.05	9.56	9.58	4.10	1.32	6.77
	r					0.97	0.99	0.99
	O	7.32	6.65	7.81	2.41	3.58	0.76	1.74
	S	7.80	7.17	7.80	2.52	3.74	1.09	5.07
COCH$_3$	Se	8.02	7.43	8.52	2.51	3.96	1.14	5.54
	Te	8.44	8.00	9.41	2.52	4.22	1.16	6.78
	r					0.87	0.99	0.99
	O	7.24	6.59	7.76		3.53	0.88	1.72
	S	7.80	7.15	7.78	9.56	3.67	1.16	5.03
COOH	Se	8.03	7.37	8.42	10.53	3.90	1.26	5.50
	Te	8.53	7.93	9.40	10.81	4.20	1.34	6.76
	r					0.85	0.99	0.99
	O	7.23	6.61	7.79	3.86	3.50	0.83	1.74
	S	7.74	7.09	7.66	3.85	3.69	1.20	4.97
COOCH$_3$	Se	8.00	7.37	8.42	3.82	3.93	1.22	5.50
	Te	8.49	7.92	9.38	3.78	4.11	1.33	6.79
	r					0.90	0.99	0.99
	O	6.43	6.39	7.55	2.38	3.26	0.88	1.98
	S	7.07	6.96	7.40	2.45	3.60	1.26	5.36
SCH$_3$	Se	7.18	7.17	8.08	2.50	3.70	1.23	5.77
	Te	7.42	7.55	8.81	2.50	4.03	1.28	6.93
	r					0.94	0.97	0.99
	O	6.25	6.31	7.40	4.90	3.30	0.86	1.80
	S	6.91	6.88	7.21	4.67	3.40	1.11	5.14
CH$_2$OH	Se	7.05	7.11	7.90	4.82	3.50	1.18	5.59
	Te	7.41	7.64	8.77	4.74	3.88	1.25	6.83
	r					0.83	0.99	0.99

In the furan, thiophene, and selenophene series, we have recently finished an extensive study of representative 2- and 3-substituted derivatives, and have found that certain ^{13}C shifts can be excellently correlated with the reactivity constants $\mathscr{F}$ and $\mathscr{R}$ of Swain and Lupton.[12]

^{1}H NMR SPECTRA

The ^{1}H NMR spectra of tellurophene, 2-acetyltellurophene, and 2-tellurophene carboxylic acid in deuteriochloroform solution have been described earlier.[13] Assignments of chemical shifts in tellurophene were based on analogy with thiophene and selenophene and on shift effects caused by substituents. In order to

obtain comparable ^{1}H NMR data for the six derivatives of the four heterocycles discussed in this paper, the spectra were recorded in deuterioacetone solutions.

In those cases when the substituent was electron-attracting the absorptions of the aromatic hydrogens were well separated, while the 2-hydroxymethyl and 2-methylthio compounds showed more strongly coupled spectra for the β-hydrogens. The refined δ and J values were obtained iteratively using an extended version of the QCPE program UEAITR (No. 188). The original version of UEAITR is given in Ref. 14. After a preliminary estimate of the parameters the calculations were performed until the best least squares fit was ob-
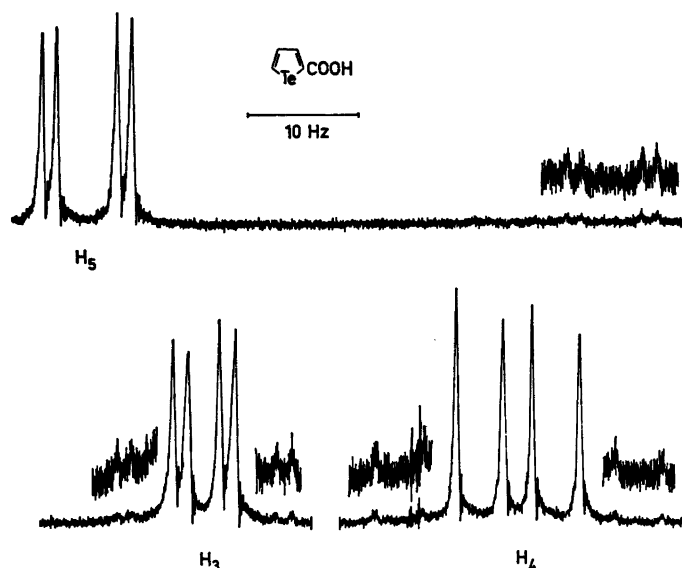
Fig. 1. ¹H NMR spectrum of 2-tellurophene carboxylic acid in deuterioacetone solution at 100 MHz showing tellurophene satellites.

Table 2. Heteroatom-hydrogen coupling constants for some 2-substituted tellurophenes and selenophenes.

Substituent	J_{Te-H_3}	J_{Te-H_4}	J_{Te-H_5}	$J_{Se-H_3}{}^a$	$J_{Se-H_4}{}^a$	J_{Se-H_5}
CHO	9.5	14.0	94.2	4.7	7.4	45.6
COCH₃	11.0	13.0	91.7	6.6	10.0	44.8
COOH	10.1	14.7	93.5	5.2	7.4	45.2
COOCH₃	14.1	16.7	97.6	–	–	44.8
SCH₃	9.7	14.9	94.7	–	–	46.1
CH₂OH	15.2	16.6	97.1	–	–	46.7

a Determined from ⁷⁷ Se spectra.

tained (RMS 0.02) The procedure resulted in calculated proton spectra with average deviations from the observed frequencies of 0.01 Hz or less.

The shifts and coupling constants are given in Table 1.

The ¹H NMR tellurophene spectrum showed satellite spectra due to ¹³C as well as ¹²⁵Te. A representative spectrum showing tellurophene satellites are given in Fig. 1. Thus, the magnitude of the coupling between the heteroatom and the three ring-hydrogens could be observed, as previously done for selenophene.[15] The measurement conditions for the two heteroatoms are comparable, they are of the same natural

abundance and the sensitivity of selenium is about half that of tellurium. The absolute values of the tellurium-hydrogen couplings of the tellurophene derivatives are given in Table 2. The same relative order $|J_{X-H_5}| \gg$ $|J_{X-H_4}| \sim |J_{X-H_3}|$ was found for some seleno-phene derivatives.[15] For each compound the magnitude of J_{X-H_4} is, however, larger than that of J_{X-H_3}.

The intervals for the largest heteroatom-hydrogen coupling, $|J_{X-H_5}|$, are $91.7 - 100.4$ Hz and $44.8 - 48.5$ Hz for the tellurophene and selenophene derivatives, respectively. There is a simple relation between coupling constants involving various isotopic nuclear species,

and the J value for a pair of nuclei.[16] The magnitudes of coupling constants between different nuclei are often compared by means of their reduced coupling constants, K,[17] defined as

$$K = (4\pi^2/\hbar\gamma_A\gamma_B)J_{AB}$$

The products of the magnetogyric ratios $\gamma_{Se}\gamma_H$ and $\gamma_{Te}\gamma_H$ are of opposite signs. By introducing the visual α-coupling constants for unsubstituted tellurophene and selenophene, 100.4 Hz and 47.5 Hz, respectively, the reduced coupling constants were calculated to be $K_{Se-H} = |2.07|$ and $K_{Te-H} = |2.64|$. As the magnitudes are of the same order the same type of coupling mechanism seems to operate in both cases. The small difference might be due to the deviation in geometry for the two five-membered rings.

From Table 2 it is obvious that there is no systematic variation in the coupling constants due to the substituents.

From the ^{13}C satellite spectrum in the ^{1}H NMR spectrum of tellurophene, the $^{13}C - H_\alpha$

and $^{13}C - H_\beta$ couplings were determined to be 183 Hz and 159 Hz, respectively. This is in agreement with the data for the other three heterocycles, where $^{13}C - H_\alpha$ is also found to be larger than $^{13}C - H_\beta$.[6]

^{13}C NMR SPECTRA

The ^{13}C NMR spectra were also recorded in deuterioacetone solution and the shifts were determined from the proton-decoupled spectra. The assignment of the α- and β-carbons in unsubstituted tellurophene was established from the undecoupled spectrum and based on the magnitude of the direct couplings. The smaller splitting was recognized in the low field ^{13}C absorption in the tellurophene spectrum. Thus the relative order of the carbon chemical shifts is opposite that of the hydrogens.

In the 2-substituted derivatives, the quaternary 2-carbon is directly identified by its lower intensity and the absence of the direct coupling, and the 5-carbon by the largest direct
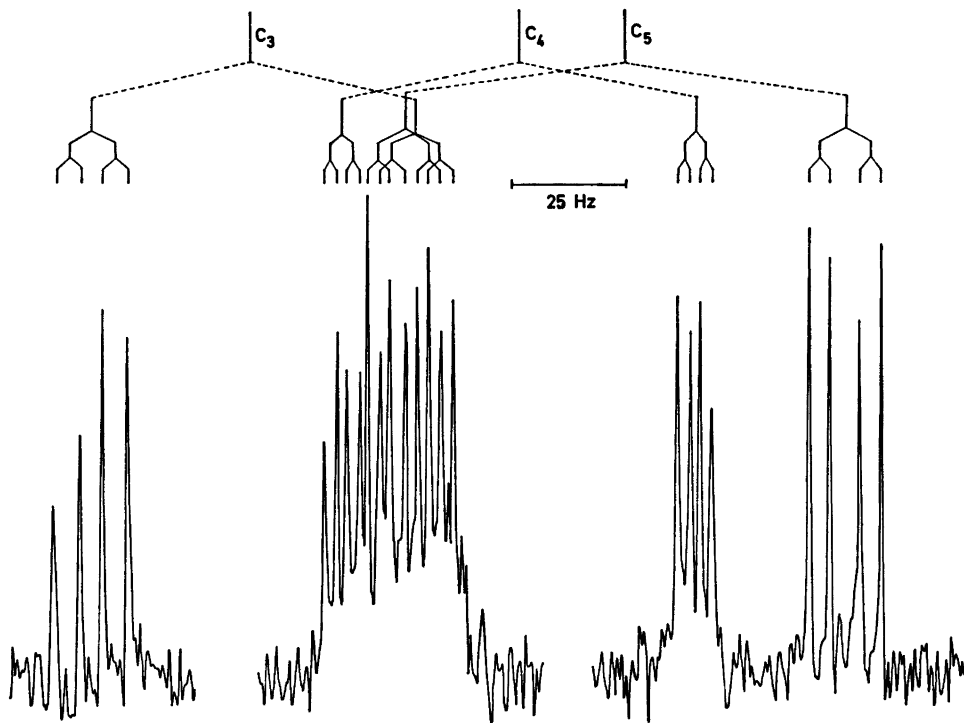

Fig. 2. [13]C spectrum of 2-methyl tellurophene carboxylic acid in deuterioacetone solution.

Table 3. ^{13}C-NMR data for some 2-substituted tellurophenes in deuterioacetate solution at 25.14 MHz using tetramethylsilane as internal standard.

Substituent	C_2	C_3	C_4	C_5	$J_{C_5-H_3}$	$J_{C_5-H_4}$	$J_{C_5-H_5}$	$J_{C_4-H_4}$	$J_{C_4-H_5}$	$J_{C_4-H_5}$	$J_{C_3-H_3}$	$J_{C_3-H_4}$	J_{C_4-H}	C_x
CHO	151.5	148.1	139.4	138.7	161	163	184	5.6	11.0	2.5	4.5	4.9	11.2	C=O 188.3
COCH₃	153.5	143.4	139.8	137.8	161	163	182	5.3	10.7	2.5	4.7	4.6	10.8	C=O 194.7 CH₃ 24.9
COOH	137.6	144.7	138.6	138.1	159	161	183	5.6	11.0	2.4	4.8	5.0	10.8	C=O 167.8
COOCH₃	139.0	144.5	138.6	137.4	164	163	184	5.6	10.7	3.0	5.0	4.8	11.2	C=O 167.1 CH₃ 52.5
SCH₃	142.1	136.3	137.8	125.6	161	161	185	6.0	10.5	2.7	5.0	4.0	11.0	CH₃ 23.5
CH₂OH	155.3	132.2	137.4	124.9	158	160	183	5.8	10.8	3.0	4.9	5.0	10.6	CH₂ 65.2

coupling. The assignments of the 3- and 4-carbons are based on the expected substituent shift effects, as compared with those obtained for benzene,[18] thiophene,[12] and selenophene derivatives.[12] The assignments thus obtained for the 3- and 4-carbons are also supported by considerations of the long-range couplings. By other ^{13}C measurements it has namely been demonstrated that the long-range coupling over three bonds ([3]J) is generally larger than [2]J.[8] This is also the case for 2-substituted thiophenes and selenophenes,[12] where it was proven by a study of deuterated derivatives. On the other hand, furans seem to be an exception to this rule.[12]

The undecoupled spectra of the tellurophene derivatives studied in this paper were of first order. In addition to the large splitting, J_{C-H}, each of the unsubstituted carbons appears as two quartets as a result of long-range couplings. These quartets overlap only in one case, namely that of methyl 2-tellurophenecarboxylate. Still all coupling could be obtained as shown in Fig. 2. The ^{13}C parameters are given in Table 3.

DISCUSSION

The difference in the proton chemical shifts of the α- and β-hydrogens in these five-membered heterocyclics has been suggested as a criterion of aromaticity. In the pure liquids the following differences were found: thiophene (0.132), selenophene (0.569), tellurophene (0.957), and furan (1.061).[19] This order is in agreement with that of decreasing aromaticity based on several criteria.[19]

The same general trend is observed in 20 % deuterioacetone solutions, except for an inversion between furan and tellurophene (*cf.* Table 4). However, a closer analysis of the

Table 4. α- and β-Hydrogen shifts (ppm) for furan, thiophene, selenophene, and tellurophene in deuterioacetone solution using TMS as internal standard.

Heteroatom	δ_α	δ_β
O ($E = 3.5$)	7.46	6.36
S ($E = 2.5$)	7.40	7.10
Se ($E = 2.4$)	8.10	7.33
Te ($E = 2.1$)	8.97	7.79
Correlation coefficient	0.81	0.999

shifts indicates that the β-hydrogen shifts vary systematically with the $+M$ effect of the heteroatom $O > S > Se > Te$, and give a good correlation with the Pauling electronegativity data for the heteroatoms ($O = 3.5$, $S = 2.5$, $Se = 2.4$, $Te = 2.1$; $r = 0.99$). The α-hydrogen shifts, on the other hand, vary irregularly, and this is probably due to the fact that in addition to electronic effects, the anisotropy of the heteroatom also plays an important role in determining the α-shifts. In all four systems, however, the α-hydrogen resonances occur at lower field than the corresponding β-hydrogen resonances.

The shift differences are even more pronounced in the ^{13}C spectra, but it is only the magnitudes of the differences between the α- and β-carbon shifts that follow the expected aromaticity order: thiophene |1.7|, selenophene |1.7| tellurophene |11.0|, and furan |33.2|. (*Cf.* Table 5, where the ^{13}C parameters for benzene also are given.) The real differences of the ^{13}C shifts, however, show no relation to aromaticity. The resonances of the α-carbons of furan and selenophene occur at lower field than those of the β-hydrogens, while the opposite is true for thiophene and tellurophene.

Table 5. α- and β-^{13}C NMR parameters for furan, thiophene, selenophene, and tellurophene in deuterioacetone solution using TMS as internal standard.

Heteroatom	C_α	C_β	$^1J_{C-H\alpha}$	$^1J_{C-H\beta}$
O	143.6	110.4	201	175
S	125.6	127.3	185	168
Se	131.0	128.8	189	166
Te	127.3	138.0	183	159
Benzene	128.7		159	

Table 6. Chemical shifts (ppm) of the ring protons of some furans, thiophenes, selenophenes, and tellurophenes relative to the α- and β-hydrogens in the parent compounds in deuterioacetone solution.

Substituent Heteroatom	CHO $\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_5$	COCH$_3$ $\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_5$	COOH $\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_5$	COOCH$_3$ $\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_6$	SCH$_3$ $\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_6$	CH$_2$OH $\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_5$
O	1.09	0.37	0.48	0.96	0.29	0.36	0.87	0.23	0.30	0.86	0.25	0.33	0.07	0.03	0.09	-0.12	-0.06	-0.05
S	0.84	0.20	0.56	0.71	0.07	0.40	0.70	0.05	0.38	0.65	0.00	0.25	-0.03	-0.13	-0.01	-0.19	-0.22	-0.19
Se	0.85	0.21	0.58	0.70	0.11	0.41	0.71	0.05	0.32	0.67	0.04	0.32	-0.14	-0.16	-0.02	-0.28	-0.21	-0.20
Te	0.83	0.26	0.59	0.65	0.21	0.44	0.74	0.14	0.43	0.70	0.13	0.41	-0.37	-0.24	-0.16	-0.38	-0.15	-0.20
Correlation Coefficient	0.97	—	0.99	0.99	—	0.97	—	—	—	—	—	—	0.84	0.99	0.88	—	—	0.97

Furthermore, the α-carbon shifts vary irregularly and are quite similar for thiophene, selenophene, and tellurophene. The β-carbon shifts, on the other hand, are systematically shifted upfield with increasing $+M$ effect of the heteroatom, and are again linearly correlated with the electronegativity of the heteroatoms ($r = 0.998$: $C_\beta = -18.9\ E_x$).

Good correlations were also obtained between the electronegativity of the heteroatoms and the magnitude of the couplings $^1J_{C-H\alpha}$ ($r = 0.96$) and $^1J_{C-H\beta}(r = 0.94)$. It is generally accepted that the direct $^{13}C-H$ couplings are related to the amount of s-character on the carbon nucleus and to the electronegativity of the substituents, the coupling constant increasing with electronegativity. This is for instance evident for the trans J_{CH} coupling in vinyl derivatives,[20] and has also been observed in acetylenic systems.[21]

Good linear correlations are also observed between shifts and coupling constants. Both C_α versus $^1J_{C-H\alpha}$ and C_β versus $^1J_{C-H\beta}$ give $r = 0.98$. For the proton shifts, an acceptable correlation was only obtained for C_β versus $^1J_{C-H\beta}$.

The absence of a linear correlation between the α-proton shift ($\delta_{H\alpha}$) and $^1J_{C-H\alpha}$ could be expected. Goldstein and Reddy[22] have used deviations from linear correlations between proton chemical shifts and $^{13}C-H$ coupling constants to estimate diamagnetic anisotropy effects. They assumed that in the absence of diamagnetic anisotropy effects and medium effects a linear correlation would be obtained. This was also the case for vinyl derivatives, while benzene and thiophene showed deviations of 78 Hz and 40 Hz, respectively (at 40 MHz). Goldstein and Reddy ascribed these deviations to anisotropy effects of the ring-current type. A preliminary study of the other five-membered heterocycles showed that the deviation form the "vinyl" line was even greater for selenophene, and for tellurophene especially great. This fact and the different behaviour of α- and β-hydrogens indicate strongly that other contributions to anisotropy than ring-current effects are responsible for the deviations. The good linear correlation between ^{13}C shifts and direct $C-H$ couplings again illustrates the fact[23-25] that carbon shifts are much less influenced by diamagnetic anisotropy effects

than the proton shifts.

Galasso [26] has recently carried out CNDO/2 calculations on the four chalcogen heterocyclics. The total charge densities at the α- and β-carbons obtained by him gave the following good linear correlations against the ^{13}C shifts: $C_{\alpha} = 74.3q + 129.3$ $(r = 0.974)$; $C_{\beta} = 532.8q + 161.7$ $(r = 0.998)$.

The proton-proton coupling constants J_{45} and J_{35} are very sensitive to a change of the heteroatom, and excellent linear correlations are obtained for all six derivatives (*cf.* Table 1). Similar observations have previously been made in vinylic systems [27] and 2-substituted thiophenes. [28] Also the coupling J_{34} increases with decreasing electronegativity. However, the correlations are not as good as for J_{45} and J_{35} and the sensitivity to changes in electronegativity is not as great.

The proton shifts relative to those of the α- and β-hydrogens of the parent compounds are given in Table 6, and the corresponding ^{13}C shifts in Table 7. The ^{13}C values for the furans, thiophenes, and selenophenes are taken from Ref. 12.

Even if the data unfortunately are limited, interesting differences between the four ring systems can be observed. The ease of transmission of the substitution resonance effects to the 5-hydrogen and 5-carbon increased in the series furan < thiophene < selenophene < tellurophene. As good correlations were obtained for the 5-proton shifts against the 5-carbon shifts in all four systems $(r > 0.97)$, the same transmission mechanism seems to be operating both for carbon and proton. This sensitivity of the 5-position to substituent effects from the 2-position indicates that the heavier chalcogens transmit the substituent effects more efficiently, which may be due to the fact that the d-orbitals are easily polarisable. Obviously more material is needed in order to place this hypothesis on a firmer basis. However, the efficient transmission of the heavier heteroatoms to the 5-position can hardly be related to the aromaticity in these systems (*cf.* Ref. 3).

The resonance of the 2-carbon was shifted as a function of both the substituent inductive effect and the $+M$ effect of the heteroatom, giving good correlations (*cf.* Table 7). The shifts of the 3- and 4-carbons caused by the substituents decreased steadily on going from furan

to tellurophene. For each type of substituent we carried out linear correlations between the ^{13}C shifts and the electronegativity of the heteroatom. Very good correlations were observed for all ring carbons in compounds containing $-I-M$ substituents, except for C_4 in the 2-acetyl series. For electron-donating substituents, correlations with electronegativity were only observed for the C_3 and C_4 resonances (*cf.* Table 7). Our data are of course too limited to decide if these deviations are due to different transmittance mechanisms for electron-attracting and electron-donating groups. It has been suggested that such differences exist. [3]

A comparison of Tables 6 and 7 shows that the 3- and 4-proton did not vary in the same systematic way as the corresponding carbons with the electronegativity of the heteroatom. This observation reflects the difference between ^{1}H and ^{13}C with regard to the ring current effect, anisotropy contribution and shift range.

Good correlations between the carbonyl ^{13}C shifts with electronegativity of the heteroatom have been obtained. This was also the case when the methyl of the methylthio and carbomethoxy group and the hydroxymethyl group were correlated with electronegativity. Only the methyl of the acetyl group fails to give such correlation (*cf.* Table 7).

Attempts were made to correlate the various ^{1}H and ^{13}C shifts with each other. The linear correlations obtained when the relative shifts of the furans, selenophenes, and tellurophenes reported in Tables 6 and 7 were plotted *versus* the relative shifts of the thiophenes are given in eqns. $1-9$ for protons and $10-21$ for carbons.

[1]H

$$\Delta H_O^3 = 1.16 \Delta H_S^3 + 0.10; \quad r = 0.99 \qquad \text{(eqn. 1)}$$

$$\Delta H_{Se}^3 = 1.11 \Delta H_S^3 - 0.08; \quad r = 0.99 \qquad \text{(eqn. 2)}$$

$$\Delta H_{Te}^3 = 1.29 \Delta H_S^3 - 0.22; \quad r = 0.99 \qquad \text{(eqn. 3)}$$

$$\Delta H_O^4 = 1.07 \Delta H_S^4 + 0.19; \quad r = 0.98 \qquad \text{(eqn. 4)}$$

$$\Delta H_{Se}^4 = 1.06 \Delta H_S^4 + 0.01; \quad r = 0.99 \qquad \text{(eqn. 5)}$$

$$\Delta H_{Se}^4 = 1.24 \Delta H_S^4 + 0.06; \quad r = 0.91 \qquad \text{(eqn. 6)}$$

$$\Delta H_O^5 = 0.68 \Delta H_S^5 + 0.10; \quad r = 0.98 \qquad \text{(eqn. 7)}$$

$$\Delta H_{Se}^5 = 1.02 \Delta H_S^5 + 0.00; \quad r = 0.99 \qquad \text{(eqn. 8)}$$

$$\Delta H_{Te}^5 = 1.17 \Delta H_S^5 - 0.02; \quad r = 0.97 \qquad \text{(eqn. 9)}$$

Table 7. Chemical shifts (ppm) of the carbons of some furans, thiophenes, selenophenes, and tellurophenes relative to the α- and β-carbons in the parent compounds in deuterioacetone solution, and ^{13}C-shifts of side-chain carbons. (X = heteroatom and r = correlation coefficient for correlation with electronegativity.)

Substituent	X	ΔC_2	ΔC_3	ΔC_4	ΔC_5	$C_{C=O}$[a]	C_{CH_3}[a]
	O	10.7	12.1	3.2	5.9	178.6	
	S	19.3	10.1	1.9	10.0	183.4	
CHO	Se	20.1	10.5	1.8	10.6	184.8	
	Te	24.2	10.1	1.4	11.5	188.3	
	r	0.99	0.96	0.99	0.99	0.97	
	O	10.3	7.9	2.8	4.3	186.7	26.2
	S	19.8	6.2	1.6	8.8	190.4	26.7
COCH$_3$	Se	21.0	5.9	1.6	9.4	191.4	26.0
	Te	26.3	5.4	1.8	10.5	194.6	24.9
	r	0.99	0.99	0.90	0.99	0.99	—
	O	2.3	8.8	2.5	4.3	160.2	
	S	9.1	7.0	1.3	7.9	163.4	
COOH	Se	9.1	6.9	1.2	8.8	164.8	
	Te	10.3	6.7	0.6	10.9	167.8	
	r	0.99	0.99	0.99	0.98	0.94	
	O	2.1	8.4	2.5	4.2	159.5	52.1
	S	8.8	6.9	1.5	8.0	162.9	52.4
COOCH$_3$	Se	9.3	6.6	1.1	8.6	163.9	52.3
	Te	11.7	6.4	0.6	10.1	167.1	52.5
	r	0.99	0.99	0.99	0.99	0.95	0.94
	O	4.7	4.1	1.8	2.1		18.7
	S	12.0	4.2	0.8	3.0		22.0
SCH$_3$	Se	13.2	2.1	0.4	2.3		22.5
	Te	14.8	1.7	−0.2	−0.7		23.5
	r	0.99	—	0.97	—		0.99
	O	12.1	−2.6	0.6	−0.8		57.0
	S	20.4	−2.2	−0.1	−0.3		59.5
CH$_2$OH	Se	23.0	−3.7	−0.5	−0.7		51.9
	Te	28.0	−5.8	−0.6	−2.4		65.2
	r	0.98	—	0.97	—		0.90

[a] Relative to TMS.

^{13}C

$\Delta C_O^2 = 0.81 \Delta C_S^2 - 5.05;\ r = 0.99$ \qquad (eqn. 10)

$\Delta C_{Se}^2 = 1.11 \Delta C_S^2 - 0.62;\ r = 0.99$ \qquad (eqn. 11)

$\Delta C_{Te}^2 = 1.40 \Delta C_S^2 - 1.76;\ r = 0.99$ \qquad (eqn. 12)

$\Delta C_O^3 = 1.22 \Delta C_S^3 - 0.11;\ r = 0.99$ \qquad (eqn. 13)

$\Delta C_{Se}^3 = 1.17 \Delta C_S^3 - 1.57;\ r = 0.99$ \qquad (eqn. 14)

$\Delta C_{Te}^3 = 1.37 \Delta C_S^3 - 3.84;\ r = 0.95$ \qquad (eqn. 15)

$\Delta C_O^4 = 1.28 \Delta C_S^4 - 0.75;\ r = 0.99$ \qquad (eqn. 16)

$\Delta C_{Se}^4 = 1.18 \Delta C_S^4 - 0.43;\ r = 0.99$ \qquad (eqn. 17)

$\Delta C_{Te}^4 = 1.13 \Delta C_S^4 - 0.71;\ r = 0.89$ \qquad (eqn. 18)

$\Delta C_O^5 = 0.58 \Delta C_S^5 + 0.28;\ r = 0.98$ \qquad (eqn. 19)

$\Delta C_{Se}^5 = 1.14 \Delta C_S^5 - 0.50;\ r = 0.99$ \qquad (eqn. 20)

$\Delta C_{Te}^5 = 1.56 \Delta C_S^5 - 3.05;\ r = 0.97$ \qquad (eqn. 21)

In most cases both the proton and ^{13}C shifts give good correlations (r > 0.97), the exceptions were observed for the tellurophenes. It is, however, difficult to understand why some of these lines do not pass through the origin. These relations can anyhow be used for predicting shifts of unknown selenophene and tellurophene derivatives, when those of thiophene are known. It is thus obvious that the NMR parameters of the four heterocycles show certain systematic regularities, which should be verified by an investigation of a larger and more representative number of substituted derivatives.

EXPERIMENTAL

All NMR spectra were recorded with a Varian XL-100-15 NMR spectrometer, equipped with frequency sweep, proton wide band decoupler, Fourier transform operation, and frequency counter. The transmitter frequency for ^{13}C was 25.142 MHz and for ^1H 100.01 MHz. The shifts were determined with an accuracy of ± 0.1 ppm and ± 0.005 ppm relative to TMS. The ^{13}C shifts were measured on proton decoupled spectra on 20 % solutions in CD_3COCD_3. The coupling constants were obtained with an accuracy of ± 0.02 Hz from proton spectra and ± 0.25 Hz from the ^{13}C spectra.

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