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^{19}F AND ^{1}H NMR STUDY OF FIVE-MEMBERED RING TRIFLONES AND RELATED σ-ADDUCTS. LONG RANGE FLUORINE-PROTON SPIN SPIN COUPLING.

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SUMMARY

Fluorine and proton chemical shifts for various trifluoromethylsulfonyl thiophene, selenophene, furan and N-methylpyrrole derivatives are reported and compared with those for nitro analogs. The ^{19}F chemical shift of the SO_2CF_3 group is found to be insensitive to its ring position as well as to the nature of the heterocycle. It is also unaffected by the loss of aromaticity and the presence of a negative charge which result from a nucleophilic addition to the ring. In most triflones studied, long range fluorine-proton coupling constants are observed but the proton involved in these couplings depends upon the α or β position of the SO_2CF_3 group as well as the nature of the ring heteroatom.

INTRODUCTION

In continuation of our studies of the effect of the SO_2CF_3 group [1-3], the strongest neutral electron-withdrawing group known [4-10], on the course of nucleophilic heteroaromatic substitution reactions, we have recently reported the synthesis of the thienyl, selenophenyl and pyrrolyl trifluoromethylsulfones (Id-h), (IId,e,g,h) and (IIId,e) and looked at the kinetics of the reactions of some of these substrates with methoxide ion in methanol [11]. In agreement with known reactivity patterns in these

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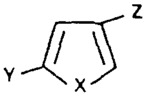
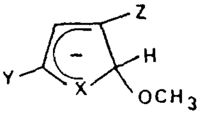
heterocyclic series [12,13], 2,4-disubstituted pyrroles were found to be unreactive while thiophene and selenophene analogs added CH_3O^- at the unsubstituted α-position to give σ-adducts (Vg,h) and (VIg,h). Concomitant studies by NMR have allowed a full characterization of (Vg) and (V,h) but not of the other adducts which decompose very rapidly, probably because of methanolysis of the SO_2CF_3 group(s) [3].

In the present paper we report and discuss unpublished ^{19}F and ^{1}H NMR data pertaining to the aforementioned species as well as to the trifluoromethyl sulfides (Ia-c) used as precursors in the thiophene series. For purpose of comparison, data for the trifluoromethylsulfonylfurans (IVd,e) and for various nitro derivatives are also presented.



(I) X=S
(II) X=Se
(III) X=N-Me
(IV) X=0



(V) X=S
(VI) X=Se

a $Y=SCF_3$, Z=H
b Y=H, $Z=SCF_3$
c $Y=Z=SCF_3$

d $Y=SO_2CF_3$, Z=H
e Y=H, $Z=SO_2CF_3$
f $Y=Z=SO_2CF_3$
g $Y=SO_2CF_3$, $Z=NO_2$
h $Y=NO_2$, $Z=SO_2CF_3$

i $Y=NO_2$, Z=H
j Y=H, $Z=NO_2$
k $Y=Z=NO_2$

RESULTS AND DISCUSSION

^{1}H NMR spectra of the 2- and 3- monosubstituted derivatives in Me_2SO-d_6 are of the AMX type and assignments of the various protons were deduced from the observed coupling constants. In the case of the 2,4-disubstituted derivatives, the proton spectra are of the AB type and the signals were attributed on the basis of the additivity of substituent effects on chemical shifts [14]. The observation of the satellite lines due to the ^{77}Se isotope in the spectra of the 2,4-disubstituted selenophenes (IIg) and (IIk) confirmed the assignments deduced from additivity arguments [15].

The spectra of most aforementioned compounds show that at least one of the ring protons is coupled with the three fluorine nuclei of the SO_2CF_3 or SCF_3 group. The recognition of the proton involved in the J_{FH}

coupling constant was deduced from the previous assignments. Moreover, when X=N-Me, a coupling between the methyl and ring protons was observed. Irradiation of the N-methyl signal allowed a distinction between the J_{FH} and J_{NMe-H} couplings to be made. All the results are summarized in Tables 1-4.

^{19}F Chemical Shifts and J_{HF} Coupling Constants

Comparison of the fluorine chemical shifts for the 2- and 3-trifluoromethylthienyl sulfides (Ia) and (Ib) in Table 1 reveals that a SCF_3 group resonates at higher field when it is located in the 2- rather than in the 3- position. This observation was used to assign the two SCF_3 resonances of the 2,4-SCF_3 derivative (Ic). In contrast, inspection of Tables 1-4 shows that not only the ring position but also the nature of the heteroatom has essentially no effect on the fluorine chemical shift of a SO_2CF_3 group. More significantly, we note that the formation of a negatively charged σ-adduct has no appreciable influence on the shift values, e.g. δ_F = -78.2 ppm for (Vg) and -79.0 ppm for (Vh). This result probably reflects the fact that a SO_2CF_3 group is a much less effective conjugating group than a sulfur one.

Going from a SCF_3 to a SO_2CF_3 group results in a high-field shift of the fluorine resonance, which is in the range 34-36 ppm. Such values compare well with data previously reported in benzene series by Sheppard et al. [4,5] and Yagupolskii et al. [16,17]. Our data for (Ia) and (Id) are also in agreement with results reported by Haas and Niemann [18] using C_6F_6 as the solvent.

For 2-trifluoromethylthiothiophene (Ia), a weak coupling between the fluorine nuclei and the H_3 proton is observed while for the 3-SCF_3 isomer (Ib), there is an interaction with both H_2 and H_4 in adjacent positions. It follows that the fluorine signal is broader when the SCF_3 group is in the 3-position, providing support for our assignment of the fluorine resonances observed in the disubstituted derivative (Ic).

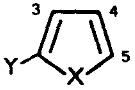
In all triflones studied, a long range $^5J_{FH}$ coupling constant is observed between the fluorine nuclei of a 3-SO_2CF_3 substituent and the H_4 proton in the adjacent β-position ; no coupling involving H_2 was resolved. Similarly, the spectra of 2-SO_2CF_3-thiophene and -selenophene (Id) and (IId) indicate the existence of a long range $^5J_{FH}$ coupling constant involving the H_3 proton in the β-position. However, such a coupling is not observed in the

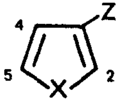
TABLE 1

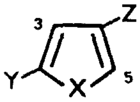
NMR Data[a] for Thiophene Derivatives and Related σ-Adducts

COMPOUND	Y	Z	$\delta_{^{19}F}$	δ_{H_2}	δ_{H_3}	δ_{H_4}	δ_{H_5}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}	J_{FH_2}	J_{FH_3}	J_{FH_4}
Ia	SCF_3	H	-44.5	-	7.60	7.23	8.01	-	-	3.7	1.3	5.4	-	0.1	n.o.
Ib	H	SCF_3	-42.5	8.16	-	7.28	7.78	1.3	3.0_5	-	-	5.0	0.1_8	-	0.4_5
Ic	SCF_3	SCF_3	Y:-44.1 Z:-42.6	-	7.85	-	8.64	-	-	-	1.5	-	-	n.r.	-
Id	SO_2CF_3	H	-78.7	-	8.25	7.52	8.60	-	-	4.0	1.4	4.9	-	0.2_6	n.o.
Ie	H	SO_2CF_3	-78.8	9.03	-	7.63	8.05	1.4	2.9_5	-	-	5.2	n.r.	-	0.4_5
If	SO_2CF_3	SO_2CF_3	Y:-78.0 Z:-78.1	-	8.93	-	9.76	-	-	-	1.7	-	-	n.r.	-
Ig	SO_2CF_3	NO_2	-77.8	-	8.83	-	9.51	-	-	-	1.8	-	-	0.2_8	-
Ih	NO_2	SO_2CF_3	-77.9	-	8.63	-	9.27	-	-	-	1.9_5	-	-	0.4	-
Ii[b]	NO_2	H	-	-	8.08	7.18	8.01	-	-	4.0	1.5	5.7	-	-	-
Ij[b]	H	NO_2	-	8.76	-	7.65	7.74	1.2	3.4	-	-	5.3	-	-	-
Ik[c]	NO_2	NO_2	-	-	8.58	-	9.05	-	-	-	2.1	-	-	-	-
Vg	SO_2CF_3	NO_2	-78.2	-	7.47	-	6.50	-	-	-	-	-	-	-	-
Vh	NO_2	SO_2CF_3	-79.0	-	7.54	-	6.13	-	-	-	0.8	-	-	0.3_6	-

[a] δ values in ppm relative to external $CFCl_3$ (^{19}F) and internal Me_4Si (^1H). Positive δ values are in the direction of increasing frequency. J values in hertz. Solvent Me_2SO-d_6. Numbering used :







[b] Ref. 24.

[c] Ref. 25.

TABLE 2

NMR data [a] for selenophene derivatives

COMPOUND	Y	Z	$\delta_{^{19}F}$	δ_{H_2}	δ_{H_3}	δ_{H_4}	δ_{H_5}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}	J_{SeH_2}	J_{SeH_5}	J_{FH_3}	J_{FH_4}
IId	SO_2CF_3	H	-78.5	-	8.45	7.72	9.23	-	-	4.1	1.4	5.3	-	46.0	0.2	n.o.
IIe	H	SO_2CF_3	-78.6	9.70	-	7.79	8.61	1.4_5	2.4_5	-	-	5.7	-	-	-	0.5_5
IIg	SO_2CF_3	NO_2	-77.7	-	8.95	-	10.00	-	-	-	1.9	-	-	37.9	0.3	-
IIh	NO_2	SO_2CF_3	-77.8	-	8.64	-	9.79	-	-	-	2.0	-	-	-	0.4_4	-
IIi[b]	NO_2	H	-	-	8.26	7.42	8.64	-	-	4.3	1.6	5.8	-	45.0	-	-
IIj[b]	H	NO_2	-	9.41	-	7.98	8.34	1.5_6	2.7_5	-	-	5.8_5	38.2	43.2_5	-	-
IIk[c]	NO_2	NO_2	-	-	8.72	-	9.51	-	-	-	2.1_7	-	-	37.7	-	-

[a] δ values in ppm relative to external $CFCl_3$ (^{19}F) and internal Me_4Si (^1H). Positive δ values are in the direction of increasing frequency. J values in Hertz. Solvent $Me_2SO\text{-}d_6$. Numbering used is the same as in Table 1.

[b] Ref. 15.

[c] Ref. 26.

TABLE 3

NMR Data [a] for N-methyl pyrrole derivatives

COMPOUND	Y	Z	$\delta_{^{19}F}$	δ_{H2}	δ_{H3}	δ_{H4}	δ_{H5}	δ_{NMe}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}	J_{NMe-H2}	J_{NMe-H5}	J_{FH_4}	J_{FH_3}
IIId	SO_2CF_3	H	-79.4	-	7.29	6.44	7.63	3.89	-	-	4.3	1.8_5	2.5_5	-	0.5	-	-
IIIe	H	SO_2CF_3	-80.1	7.93	-	6.60	7.13	3.79	1.8	2.15	-	-	3.0_5	0.5	0.3	0.3	-
IIIg	SO_2CF_3	NO_2	-78.3	-	7.93	-	8.71	3.95	-	-	-	2.0_5	-	-	0.5_5	-	-
IIIh	NO_2	SO_2CF_3	-79.3	-	7.80	-	8.45	4.06	-	-	-	2.3	-	-	0.5_7	-	0.3
IIIi	NO_2	H	-	-	7.22	6.25	7.31	3.96	-	-	4.4_4	2.0	2.6	-	-	-	-
IIIj	H	NO_2	-	7.93	-	6.67	6.89	3.72	1.9	2.3_5	-	-	3.1_5	-	-	-	-

TABLE 4

NMR Data [a] for furan derivatives

COMPOUND	Y	Z	$\delta_{^{19}F}$	δ_{H_2}	δ_{H_3}	δ_{H_4}	δ_{H_5}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}	J_{FH_4}	J_{FH_5}
IVd	SO_2CF_3	H	-78.5	-	8.08	7.06	8.49	-	-	3.8	0.9	1.7	-	0.24
IVe	H	SO_2CF_3	-79.5	9.08	-	7.14	8.19	0.9	1.5_5	-	-	1.0_5	0.4_5	-
IVi[b]	NO_2	H	-	-	7.58	6.80	7.98	-	-	4	1	2	-	-

[a] δ values in ppm relative to external $CFCl_3$ (^{19}F) and internal Me_4Si (^1H). Positive δ values are in the direction of increasing frequency. J values in Hertz. Solvent Me_2SO-d_6. Numbering used is the same as in Table 1.

[b] Ref. 27.

furan derivative (IVd). Instead, the spectra reveal a $^6J_{FH}$ coupling with H_5, maybe because of a different conformation of the 2-SO_2CF_3 group due to repulsion between a sulfonyl oxygen and the ring oxygen. It is also to be noted that J_{FH} coupling constants involving H_2 or H_5 are not resolved in the pyrrole derivatives (Table 4) ; however the signals are broadened, but this can be due to the quadrupolar relaxation of the nitrogen nucleus.

^{1}H Chemical Shifts and J_{HH} Coupling Constants

The influence of the SO_2CF_3 and NO_2 groups on the ^{1}H chemical shifts of the various 2- and 3-substituted heterocycles is illustrated in Table 5. Due to the importance of the solvent effects on ^{1}H shifts in these classes of compounds [15,19,20], all data used to calculate the $\Delta\delta$ values were obtained from experiments carried out in Me_2SO solutions. Relevant data for 3-nitrofuran are however lacking in the literature.

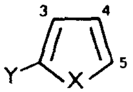
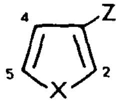
Inspection of Table 5 reveals that the influence of a 2-SO_2CF_3 group is much greater than that of a 2-NO_2 group, in agreement with the Taft and Hammett σ values reported for these substituents [5]. However, for both substituents, changes in the $\Delta\delta$ values decrease along the same sequence $\Delta\delta_3 > \Delta\delta_5 > \Delta\delta_4$. This further confirms that the 3-, 4- and 5- positions of 2-substituted five-membered ring heterocycles behave as _ortho_-, _meta_- and _para_-like positions in aromatic derivatives. Of interest is that substituent effects for H_5 decrease on going from thiophene to selenophene to furan derivatives. That this sequence parallels the order of decreasing aromaticity [21] suggests that resonance effects are predominant in determining the influence of the substituents in this position. This conclusion is in agreement with the interpretation of substituent effects on ^{13}C chemical shifts observed in these three heterocycles [22].

The situation which prevails in the 3-substituted derivatives is less clearcut since it is only in the 2- and 5-positions that a SO_2CF_3 group has a larger effect than a NO_2 group. We note, however, that the $\Delta\delta$ values for the 2-position are very important and of the order of those observed for the 3-position in the 2-substituted isomers.

In a general way, the J_{HH} coupling constants increase on introduction of an electron-withdrawing substituent in the heteroaromatic rings. This trend, which is especially apparent from Tables 1 and 2, is perhaps not surprising since it has been shown in selenophene series [15] that coupling

TABLE 5

Substituent effects on ^{1}H chemical shifts for 2- and 3-monosubstituted heterocycles[a]

	X = S			X = Se			X = NMe			X = O		
	$\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_5$	$\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_5$	$\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_5$	$\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_5$
Y = SO_2CF_3	1.14	0.41	1.13	1.10	0.37	1.06	1.33	0.48	0.96	1.60	0.58	0.83
Y = NO_2	0.97	0.07	0.54	0.91	0.07	0.47	1.26	0.29	0.64	1.10	0.32	0.32
	$\Delta\delta_2$	$\Delta\delta_4$	$\Delta\delta_5$	$\Delta\delta_2$	$\Delta\delta_4$	$\Delta\delta_5$	$\Delta\delta_2$	$\Delta\delta_4$	$\Delta\delta_5$	$\Delta\delta_2$	$\Delta\delta_4$	$\Delta\delta_5$
Z = SO_2CF_3	1.56	0.52	0.58	1.53	0.44	0.44	1.26	0.64	0.46	1.42	0.66	0.53
Z = NO_2	1.29	0.54	0.27	1.24	0.63	0.17	1.26	0.71	0.22	–	–	–

[a] ^{1}H chemical shifts for unsubstituted heterocycles (δ values in ppm from internal Me_4Si, solvent $Me_2SO\text{-}d_6$)

X = S, $\delta_{2,5}$: 7.47 $\delta_{3,4}$: 7.11 . X = Se, $\delta_{2,5}$: 8.17 $\delta_{3,4}$: 7.35

X = NMe, $\delta_{2,5}$: 6.67 $\delta_{3,4}$: 5.96 . X = O, $\delta_{2,5}$: 7.66 $\delta_{3,4}$: 6.48

constants can be correlated with the reactivity constants F and R of Swain and Lupton [23]. This accounts for the similarity of the various J_{HH} coupling constants determined for 2- or 3- nitro and trifluoromethylsulfonyl heterocycles. The substituent effects are additive [15], so that J_{35} is greater in the 2,4-disubstituted derivatives than in the monosubstituted precursors.

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