

fluorescence) is assigned to ν_3 in this compound. Although $(C_6H_5)_4AsCl$ ⁵ and $(C_6H_5)_4AsI$ ⁶ have various IR and Raman bands between 400 and 350 cm^{-1} we have tentatively attributed the bands around 360 cm^{-1} to ν_3 . No other neighboring bands in the two compounds which definitely were not cation bands were observed in this region.

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Nuclear Magnetic Resonance of Aromatic Heterocyclics. VI. The Correlation of PMR-shifts of Monosubstituted Selenophenes with Reactivity Parameters

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A recent publication by Morel *et al.*¹ on the PMR spectra of some substituted selenophenes has prompted us to publish

the results we have hitherto obtained on the correlation of the NMR spectral data of selenophenes with the reactivity constants F' and R of Swain and Lupton.² We have recently shown in an extensive study of the NMR parameters of fluorothiophenes, thiophenes, and fluorobenzenes, that the chemical shifts and coupling constants could be correlated with a linear combination of the substituent parameters F and R .³ The regression equations

$$z_k = i_k + f_k F + r_k R$$

where z_k is the NMR parameter, i_k is the intercept and f_k , r_k are the regression constants, were calculated by a linear least-squares multiple correlation computer program. In this way an estimate of the relative inductive and mesomeric contributions to the shifts and coupling constants could be obtained. The chemical shifts of the substituted selenophenes given in Table 1 were taken from Ref. 1 except those of 2-fluoro- and 2-iodoselenophene which were prepared and measured at this institute.⁴ The regression equations which were obtained are given in Table 2. It is evident that in spite of the relatively few substituents hitherto studied, and in spite of the fact that concentration dependence of the chemical shifts was not eliminated, good correlations were obtained for some of the shifts, especially those of the 2-substituted derivatives. The values of f and r are very similar to those in thiophenes.³ Morel *et al.*¹ stated that they could not obtain any simple relation between the chemical shifts and Hammett-Taft constants or electronegativity. We have, however, found that with the halogen substituents good linear relations with electronegativity are obtained.⁴ The success obtained thus far with the limited material available makes further investigations attractive. It is hoped that in this way information about the transmittance of inductive and mesomeric effects in aromatic heterocyclics can be obtained.

Experimental. NMR spectra were obtained with a Varian XL-100 spectrometer.

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Table 1. Chemical shifts of substituted selenophenes relative to the α - and β -hydrogens of selenophene in solution.

	δ_3^2	δ_4^2	δ_5^2	δ_3^3	δ_4^3	δ_5^3
OCH ₃	+1.14	+0.54	+0.88	+1.40	+0.32	+0.25
SCH ₃	+0.20	+0.20	+0.07	+0.49	+0.14	+0.06
Br	+0.07	+0.32	+0.16			
CN	-0.5	-0.037	-0.335	-0.675	-0.22	-0.17
COCH ₃	-0.48	-0.01	-0.31	-0.89	-0.52	-0.04
COOH	-0.50	-0.02	-0.30	-0.66	-0.71	-0.24
NO ₂	-0.78	-0.03	-0.38	-0.98	-0.29	+0.09
F	-0.78	+0.73	+0.50			
I	+0.16	+0.40	-0.05			
CH ₃				+0.15	+0.23	+0.54

Table 2. Regression equations relating proton chemical shift δ of monosubstituted selenophenes to substituent constants F and R .

Equation	b^b	c^c	N^d
$\delta_3^2 = (0.04 \pm 0.23) - (0.37 \pm 0.39)F - (2.21 \pm 1.04)R$	0.23	0.93	9
$\delta_4^2 = (0.01 \pm 0.14) + (0.21 \pm 0.19)F - (1.10 \pm 0.48)R$	0.12	0.91	9
$\delta_5^2 = (0.05 \pm 0.18) - (0.07 \pm 0.26)F - (1.57 \pm 0.63)R$	0.15	0.94	9
$\delta_3^3 = -(0.35 \pm 0.14) + (0.22 \pm 0.23)F - (3.43 \pm 0.42)R$	0.17	0.98	7
$\delta_4^3 = -(0.14 \pm 0.20) - (0.06 \pm 0.33)F - (1.21 \pm 0.67)R$	0.25	0.77	7
$\delta_5^3 = (0.21 \pm 0.18) - (0.28 \pm 0.30)F - (0.40 \pm 0.55)R$	0.23	0.49	7

^a The shifts are given in ppm relative to those of selenophene. The notations δ_i^2 , δ_j^3 denote the shifts of the i - and j -proton of 2- and 3-substituted selenophenes, respectively.

^b Standard deviation in ppm.

^c Correlation coefficient.

^d Number of substituents in the regression analysis.

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Synthesis of a [1,4]Oxathiano-[3,2-b]pyridine Derivative

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Studies^{1,2} of the evaporation process of S_N -quaternary salts in the mass spectrometer required for comparative purposes a [1,4]oxathiano[3,2-b]pyridine derivative to be synthesized. This ring system does not appear to have previously been described. Previous findings³ show that a 2-ethio derivative with a displaceable group on the ethyl β -carbon (IV) is cyclized with preferential 5-membered ring formation over the pyridyl nitrogen (II). Cyclisa-