Nuclear Magnetic Double-resonance Studies of Organo-selenium Compounds

By **W. McFarlane** * and **R. J. Wood**, Chemistry Department, Sir John Cass School of Science and Technology, City of London Polytechnic, Jewry Street, London E.C.3

^{1}H–{^{77}Se} Double-resonance experiments have been used to determine selenium chemical shifts in 80 organo-selenium compounds containing ^{77}Se in natural abundance. The shifts cover a range of over 1500 p.p.m. and are relatively insensitive to solvent effects. Electronegative substituents give shifts to low field, and in general the shifts parallel those found in similar phosphorus compounds, but are several times larger for a given electronic change. Correlations are found with the extent of α-chain branching in alkyl derivatives, and with Hammett σ-constants in substituted aryl derivatives. The chemical shifts show greater promise as diagnostic tools than do coupling constants involving selenium.

PROGRESS in understanding the chemical shifts of many of the heavier nuclei is impeded by lack of experimental data, although this situation is improving rapidly as better spectrometers become available. This limitation is particularly serious for elements of group VI, because neither oxygen nor sulphur has a magnetic isotope of even moderate abundance. However, both selenium and tellurium have isotopes with spin quantum number $\frac{1}{2}$ which are of reasonable natural abundance, and in this paper we report measurements of ^{77}Se ($I = \frac{1}{2}$, abundance $= 7{\cdot}6\%$) chemical shifts in a range of organo-selenium compounds. Previously, direct observation of the ^{77}Se resonance has been used [1-3] in a number of such studies, but this approach suffers from the disadvantages of the low inherent sensitivity to n.m.r. detection of ^{77}Se (only 0·7% of that of the proton in a polarising field of the same strength), and the unfavourable relaxation time of ^{77}Se in many of its compounds which necessitates the use of fast passage techniques. We have therefore used a double-resonance technique wherein a ^{77}Se satellite in the proton (or ^{19}F) spectrum is observed and the ^{77}Se resonance frequencies at which this is perturbed give the required chemical shift.[4] This technique overcomes the problems of poor sensitivity and unfavourable relaxation time, and has the additional advantage that resonances in the proton and ^{77}Se spectra may be assigned to the same species unequivocally. The precision of measurement is also markedly superior to that which is normally achieved by direct observation. Previously,[5] ^{1}H–{^{77}Se} double resonance experiments have been used to study coupling between ^{77}Se and nuclei other than ^{1}H or ^{19}F, and high resolution ^{77}Se INDOR spectra have been presented. In the present work we have endeavoured to study series of compounds in which a particular property is varied systematically so as to assess the effect upon the ^{77}Se chemical shift of specific electronic changes, and to facilitate comparison with data for group V and group VII elements.

EXPERIMENTAL

Proton and ^{19}F spectra were recorded on a JEOL C-60-H spectrometer at measuring frequencies of 60 and 56·4 MHz respectively, using 5 mm spinning-sample tubes at 23°. A Schlumberger FS-30 frequency synthesiser and tuned amplifier provided r.f. power at the ^{77}Se resonant frequency (*ca.* 11·44 MHz), and the basic spectrometer radio frequency was also derived from the frequency synthesiser. Most spectra were recorded in the field-sweep mode with field-frequency stabilisation circuitry actuated by the signal from an external water sample. A precision of better than ±1 Hz (*i.e.* 0·1 p.p.m.) was attained in the measurements of the ^{77}Se chemical shifts in this way, and where necessary greater precision could be obtained by using frequency sweep and internal field-frequency stabilisation. In order to facilitate comparison with data obtained in other laboratories the ^{77}Se chemical shifts are quoted in two forms: (*a*) as a resonance frequency corrected [4] to a polarising magnetic field of strength such that Me_4Si would give a proton resonance of exactly 100 MHz — the Ξ value, and (*b*) as a chemical-shift difference in p.p.m. to high field of dimethyl selenide.

Most of the compounds used in this work were prepared by standard methods: *Symmetrical selenides* and *di-selenides* [6] were made from the reaction between alkyl halide, selenium, and sodium formaldehyde sulphoxylate; *aryl selenols* from selenium and the appropriate Grignard reagent; [7] *alkyl selenols* by reduction of the corresponding alkyl diselenide with hypophosphorous acid; [8] *unsymmetrical selenides* from the sodium salt of a selenol and an alkyl halide; *selenonium salts* from selenide and alkyl halide—attempts to make certain of these necessitated the use of elevated temperatures which led to rearrangement reactions, *e.g.* a mixture of isopropyl bromide and dimethyl selenide gave mainly trimethyl selenonium bromide; *dialkyl selenium dihalides* from the dialkyl selenide and halogen; *seleno-esters* from the selenol and an acid chloride; [9] *unsymmetrical diselenides* and *seleno-sulphides* by mixing the appropriate symmetrical compounds.[5a]

RESULTS

In many of the compounds examined the coupling between ^{77}Se and associated protons was large enough

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^{77}Se Chemical shifts in organo-selenium compounds

No.	Compound	Ξ (^{77}Se) (Hz [a])	δ(^{77}Se) (p.p.m.) [b]	^nJ(Se–H) (Hz)	Solvent [c]
(1)[f]	$MeSeO_2H$	19,094,718 ± 8	−1216	$^2J = 13{\cdot}5 \pm 0{\cdot}2$	H_2O
(2)	$MeSeCl_3$	19,088,500 ± 50	−890	$^2J = 11{\cdot}9 \pm 0{\cdot}2$	CH_2Cl_2
(3)[f]	Me_2SeO	19,087,010 ± 8	−812	$^2J = 11{\cdot}7 \pm 0{\cdot}2$	H_2O
(4)	p-$MeOC_6H_4SeC(O)CH_3$	19,083,892 ± 2	−649	$^3J = 7{\cdot}0 \pm 0{\cdot}3$	Neat
(5)	o-$MeOC_6H_4SeC(O)CH_3$	19,083,395 ± 3	−623	$^3J = 8{\cdot}0 \pm 0{\cdot}3$	Neat
(6)[e]	o-$MeOC_6H_4SeC(O)CF_3$	19,083,253 ± 8	−615	—	Neat
(7)	$Pr^i_2SeBr_2$	19,085,665 ± 17	−742	$^3J = 12{\cdot}0 \pm 0{\cdot}4$	CCl_4
(8)	Et_2SeBr_2	19,081,825 + 7	−540	$^3J = 18{\cdot}2 \pm 0{\cdot}3$	CCl_4
(9)	Me_2SeCl_2	19,080,075 ± 30	−448	$^2J = 10{\cdot}2 \pm 0{\cdot}2$	CH_2Cl_2
(10)	Me_2SeBr_2	19,078,940 ± 30	−389	$^2J = 10{\cdot}0 \pm 0{\cdot}2$	CH_2Cl_2
(11)[d]	PhSeSMe	19,081,320 ± 3	−514	$^3J = 4{\cdot}5 \pm 0{\cdot}2$	See text
(12)	$Bu^t_2Se_2$	19,080,932 ± 30	−493	$^3J = 11{\cdot}4 \pm 0{\cdot}3$	Neat
(13)	$Pr^i_2Se_2$	19,079,285 ± 2	−407	$^2J = 11{\cdot}4 \pm 0{\cdot}2$	Neat
(14)	$(PhCH_2)_2Se_2$	19,079,197 ± 17	−402	$^2J = 14{\cdot}3 \pm 0{\cdot}3$	CH_2Cl_2
(15)	Et_2Se_2	19,077,995 ± 3	−339	$^3J = 10{\cdot}2 \pm 0{\cdot}3$	Neat
(16)	Me_2Se_2	19,076,707 ± 2	−275	$^2J = 11{\cdot}9 \pm 0{\cdot}2$	Neat
(17)	Pr^i_2Se	19,079,808 ± 17	−436	$^3J = 10{\cdot}1 \pm 0{\cdot}2$	Neat
(18)	$MeSeBu^t$	19,077,133 ± 8	−294	$^2J = 9{\cdot}8 \pm 0{\cdot}2$ $^3J = 10{\cdot}5 \pm 0{\cdot}3$	CH_2Cl_2
(19)	Et_2Se	19,075,975 ± 17	−233	$^3J = 10{\cdot}3 \pm 0{\cdot}3$	Neat
(20)	MeSeEt	19,073,583 ± 20	−108	$^2J = 9{\cdot}0 \pm 0{\cdot}2$	CH_2Cl_2
(21)	Me_2Se	19,071,523 ± 2	0	$^2J = 10{\cdot}5 \pm 0{\cdot}2$	Neat
(22)	Bu^tSeH	19,076,828 ± 30	−278	$^1J = 38 \pm 1$	CH_2Cl_2
(23)[g]	$PhCH_2SeH$	19,073,573 ± 2	−107	$^1J = 43 \pm 1$	CH_2Cl_2
(24)	EtSeH	19,072,323 ± 17	−42	$^1J = 44 \pm 1$	Neat
(25)[h]	MeSeH	19,069,317 ± 2	+116	$^1J = 44 \pm 1$ $^2J = 9{\cdot}4 \pm 0{\cdot}2$	Neat
(26)	$Bu^tSe^-Na^+$	19,073,987 ± 30	−129	$^3J = 8{\cdot}4 \pm 0{\cdot}2$	H_2O
(27)	$Pr^{i-}SeNa^+$	19,071,690 ± 8	−8·7	$^3J = 8{\cdot}6 \pm 0{\cdot}3$	H_2O
(28)	$EtSe^-Na^+$	19,068,660 ± 17	+150	$^3J = 9{\cdot}0 \pm 0{\cdot}3$	H_2O
(29)	$MeSe^-Na^+$	19,065,192 ± 17	+332	$^2J = 6{\cdot}6 \pm 0{\cdot}2$	H_2O
(30)	$Me_3Se^+I^-$	19,076,340 ± 17	−253	$^2J = 8{\cdot}0 \pm 0{\cdot}4$	H_2O
(31)	$Me_2EtSe^+I^-$	19,077,080 ± 50	−291	$^2J = 8{\cdot}0 \pm 0{\cdot}3$	H_2O
(32)	$Et_3Se^+I^-$	19,078,710 ± 17	−377	$^3J = 17{\cdot}3 \pm 0{\cdot}4$	H_2O
(33)[h]	p-$MeOC_6H_4Se^+Me_2I^-$	19,077,728 ± 17	−325	$^2J = 9{\cdot}3 \pm 0{\cdot}3$	H_2O
(34)	PhSeH	19,074,417 ± 1	−152	$^1J = 56 \pm 1$	Neat
(35)	m-$CF_3C_6H_4SeH$	19,074,560 ± 1	−159	$^1J = 55{\cdot}5 \pm 0{\cdot}5$	Neat
(36)	o-FC_6H_4SeH	19,075,157 ± 8	−191	$^1J = 58{\cdot}5 \pm 0{\cdot}5$	Neat
(37)	m-Fe_6H_4SeH	19,074,643 ± 3	−164	$^1J = 57{\cdot}2 \pm 0{\cdot}4$	Neat
(38)	p-FC_6H_4SeH	19,074,212 ± 2	−141	$^1J = 56 \pm 1$	Neat
(39)	o-ClC_6H_4SeH	19,074,537 ± 7	−158	$^1J = 61 \pm 1$	Neat
(40)	m-ClC_6H_4SeH	19,074,702 ± 2	−167	$^1J = 57{\cdot}8 \pm 0{\cdot}4$	Neat
(41)	p-ClC_6H_4SeH	19,074,225 ± 8	−142	$^1J = 55{\cdot}5 \pm 0{\cdot}5$	CH_2Cl_2
(42)	o-$MeOC_6H_4SeH$	19,073,130 ± 1	−84	$^1J = 62{\cdot}0 \pm 0{\cdot}4$	Neat
(43)	m-$MeOC_6H_4SeH$	19,074,442 ± 2	−153	$^1J = 57{\cdot}8 \pm 0{\cdot}4$	Neat
(44)	p-$MeOC_6H_4SeH$	19,073,847 ± 8	−122	$^1J = 51 \pm 1$	Neat
(45)	o-CH_3CH_4SeH	19,073,657 ± 2	−112	$^1J = 57 \pm 1$	Neat
(46)	m-$CH_3C_6H_4SeH$	19,074,273 ± 8	−144	$^1J = 56{\cdot}3 \pm 0{\cdot}4$	Neat
(47)	p-$CH_3C_6H_4SeH$	19,073,968 ± 8	−128	$^1J = 55 \pm 1$	Neat
(48)	PhSeMe	19,075,377 ± 8	−202	$^2J = 11{\cdot}4 \pm 0{\cdot}2$	CH_2Cl_2
(49)	m-$CF_3C_6H_4SeMe$	19,075,652 ± 8	−217	$^2J = 10{\cdot}9 \pm 0{\cdot}2$	Neat
(50)	m-FC_6H_4SeMe	19,075,600 ± 8	−214	$^2J = 11{\cdot}5 \pm 0{\cdot}2$	CH_2Cl_2
(51)	p-FC_6H_4SeMe	19,075,330 ± 2	−200	$^2J = 10{\cdot}4 \pm 0{\cdot}3$	CH_2Cl_2
(52)	o-ClC_6H_4SeMe	19,075,352 ± 17	−201	$^2J = 12{\cdot}5 \pm 0{\cdot}2$	CH_2Cl_2
(53)	m-ClC_6H_4SeMe	19,075,630 ± 8	−215	$^2J = 11{\cdot}0 \pm 0{\cdot}3$	CH_2Cl_2
(54)	p-ClC_6H_4SeMe	19,075,393 ± 8	−203	$^2J = 10{\cdot}1 \pm 0{\cdot}2$	CH_2Cl_2
(55)	o-$MeOC_6H_4SeMe$	19,074,390 ± 8	−150	$^2J = 12{\cdot}3 \pm 0{\cdot}2$	CH_2Cl_2
(56)	m-$MeOC_6H_4SeMe$	19,075,480 ± 8	−207	$^2J = 10{\cdot}9 \pm 0{\cdot}2$	Neat
(57)	p-$MeOC_6H_4SeMe$	19,075,157 ± 17	−191	$^2J = 10{\cdot}9 \pm 0{\cdot}2$	$CDCl_3$
(58)	o-MeC_6H_4SeMe	19,074,617 ± 30	−162	$^2J = 12{\cdot}0 \pm 0{\cdot}3$	CH_2Cl_2
(59)	m-MeC_6H_4SeMe	19,075,322 ± 8	−199	$^2J = 10{\cdot}5 \pm 0{\cdot}3$	CH_2Cl_2
(60)	p-MeC_6H_4SeMe	19,075,278 ± 8	−197	$^2J = 10{\cdot}8 \pm 0{\cdot}2$	Neat
(61)	PhSeEt	19,077,750 ± 8	−327	$^3J = 12{\cdot}7 \pm 0{\cdot}2$	CH_2Cl_2
(62)	m-$CF_3C_6H_4SeEt$	19,078,000 ± 8	−340	$^3J = 13{\cdot}0 \pm 0{\cdot}3$	Neat
(63)	m-ClC_6H_4SeEt	19,077,937 ± 30	−336	$^3J = 12{\cdot}4 \pm 0{\cdot}3$	CH_2Cl_2
(64)	p-FC_6H_4SeEt	19,077,700 ± 17	−324	$^3J = 12{\cdot}4 \pm 0{\cdot}2$	CH_2Cl_2
(65)	o-$MeOC_6H_4SeEt$	19,076,523 ± 17	−362	$^3J = 12{\cdot}4 \pm 0{\cdot}2$	CH_2Cl_2
(66)	m-$MeOC_6H_4SeEt$	19,077,838 ± 17	−331	$^3J = 12{\cdot}0 \pm 0{\cdot}2$	Neat
(67)	p-$MeOC_6H_4SeEt$	19,077,588 ± 8	−318	$^3J = 12{\cdot}0 \pm 0{\cdot}2$	CH_2Cl_2
(68)	o-MeC_6H_4SeEt	19,076,790 ± 17	−276	$^3J = 11{\cdot}5 \pm 0{\cdot}3$	CH_2Cl_2
(69)	p-MeC_6H_4SeEt	19,077,692 ± 8	−323	$^3J = 12{\cdot}4 \pm 0{\cdot}3$	Neat
(70)	o-$MeOC_6H_4SePr^i$	19,078,300 ± 17	−355	$^3J = 10{\cdot}0 \pm 0{\cdot}5$	CH_2Cl_2
(71)	Pr^iSeH	19,074,553 ± 17	−159	$^1J = 43{\cdot}0 \pm 0{\cdot}3$	Neat
(72)	$EtSeCl_3$	19,090,492 ± 50	−995	$^3J = 8{\cdot}3 \pm 0{\cdot}3$	CH_2Cl_2
(73)[f]	$(MeO)_2SeO_2$	19,091,607 ± 2	−1053	$^3J = 24{\cdot}8 \pm 0{\cdot}2$	CH_2Cl_2
(74)[f]	$(EtO)_2SeO_2$	19,091,493 ± 8	−1047	$^3J = 19{\cdot}0 \pm 0{\cdot}3$	CH_2Cl_2
(75)[i]	$(MeO)_2SeO$	19,097,065 ± 2	−1339	$^3J = 7{\cdot}6 \pm 0{\cdot}2$	Neat

TABLE (*Continued*)

No.	Compound	Ξ (^{77}Se) (Hz [a])	δ(^{77}Se) (p.p.m.) [b]	^{n}J(Se–H) (Hz)	Solvent [c]
(76) [h]	PhSeSe*Me	19,077,133 ± 2	-294	$^{2}J = 12{\cdot}2 \pm 0{\cdot}2$	See text
	PhSe*SeMe	19,080,017 ± 2	-445	$^{3}J = 2{\cdot}4 \pm 0{\cdot}2$	
(77) [k]	*cis*-$(Me_2Se)_2PtCl_2$	19,073,818 ± 3	-120	$^{2}J = 10{\cdot}0 \pm 0{\cdot}2$	CH_2Cl_2
(78) [k]	*trans*-$(Me_2Se)_2PtCl_2$	19,074,102 ± 1	-135	$^{2}J = 9{\cdot}5 \pm 0{\cdot}2$	CH_2Cl_2
(79) [j]	$(CF_3Se)_2$		-528		Neat
(80) [l]	Me_2PSeMe	19,072,631	-58	$^{2}J = 10{\cdot}7 \pm 0{\cdot}2$	Neat
(81) [l]	$Me_2P(S)SeMe$	19,075,258	-195	$^{2}J = 10{\cdot}8 \pm 0{\cdot}2$	CH_2Cl_2
(82) [m]	Ph_2Se		-402		Neat
(83) [j]	H_2Se		$+226$	$^{1}J = 63{\cdot}4 \pm 0{\cdot}5$	Neat
(84) [m]	Ph_2Se_2		-460		Neat

[a] Resonant frequency at a polarising field strength appropriate to a Me_4Si proton resonance of exactly 100 MHz. [b] To high field of dimethyl selenide. [c] Neat samples contained *ca.* 5% of Me_4Si or CH_2Cl_2 to provide a locking and/or reference signal. [d] Present in mixture containing PhSeH and Me_2S_2. [e] $^{3}J(^{77}Se \cdots {}^{19}F) = 23{\cdot}6$ Hz. [f] Chemical shift and coupling constant dependent on pH of solution. The values quoted are for pH = 7. [g] See ref. 5*d*. [h] See ref. 5*a*. [i] We thank D. S. Rycroft for this measurement. [j] See ref. 2. [k] See ref. 5*c*. [l] See ref. 5*e*. [m] Taken from ref. 3.

(typically *ca.* 10 Hz) for the fine structure of ^{77}Se spectrum to be discernible in the spin-tickling [10] experiments, and a typical ^{77}Se INDOR spectrum has been reported elsewhere.[5a] Whenever this was so, care was taken to ensure that the centre of the selenium spectrum was correctly identified since an error of $\pm J(^{77}Se\text{–}H)$ in the frequency measurement would correspond to an error of *ca.* 1 p.p.m. in the ^{77}Se chemical shift at our magnetic-field strength. The concentration and solvent dependence of the ^{77}Se chemical shift in selected compounds was studied, and with the exceptions noted below was found to be less than ±1 p.p.m. and therefore insignificant compared with the total range of chemical shifts (1500 p.p.m.) found in this work. In the case of aryl and alkyl selenols variations of up to 30 p.p.m. in the ^{77}Se chemical shift were found according to the solvent used; however, large deviations were found only when solvents capable of forming hydrogen bonds with the Se–H proton of the selenol were used. Similarly, the ^{77}Se chemical shifts in compounds with direct Se=O linkages were found to be pH-dependent and the values in the table are for pH = 7.

In the compounds with at least one alkyl group attached to selenium spin coupling between ^{77}Se and the α and β protons was normally large enough (>5 Hz) for some ^{77}Se satellites to be clearly visible in the proton spectrum. However, no ^{77}Se satellites of aromatic proton resonances were ever observed, so it appears that any coupling between selenium and the ring protons is less than 5 Hz. In phenyl selenol (34) irradiation at the ^{77}Se resonant frequency (determined from observations on the Se–H proton resonance) had no perceptible effect upon the appearance of the complex aromatic proton resonance, again indicating that $J(^{77}Se\text{–}H_{Aromatic}) < 5$ Hz. The precision with which ^{77}Se line positions could be determined was only ±2 Hz in this compound, however, so the coupling is apparently not zero. This conclusion was confirmed by Freeman and Gestblom's double-resonance technique [11] for the 'transfer of fine structure.' The ^{77}Se spectrum consists of two multiplets separated by $^{1}J(^{77}Se\text{–}H) = 56$ Hz, and irradiation at the centre frequency of either of these with an r.f. field of strength given by $\gamma(^{77}Se)B_2/2\pi = 12$ Hz split each of the satellites of the Se–H proton resonance into two multiplets. The fine structure appearing in these corresponds to the fine structure of the ^{77}Se spectrum (with all splittings halved) and although the resolution was inadequate to permit full analysis it was clear that $^{3}J(^{77}Se\text{–}H_{ortho}) =$ *ca.* 3 Hz. The data are given in the Table.

DISCUSSION

It is generally accepted that the magnetic shielding of the heavier nuclei is dominated by Ramsey's [12] paramagnetic term σ^{p}, which for selenium will be given by equation (1) where ΔE is a mean excitation energy, and

$$\sigma^{p} = -(\Delta E)^{-1}(Q_{4p} + Q_{4d}) \qquad (1)$$

Q_{4p} and Q_{4d} are related to the electron imbalance in the *p* and *d* valence orbitals of the selenium atom.[13] In many selenium compounds Q_{4d} may be ignored, and ΔE may be taken as approximately constant for members of a related series, so that changes in the selenium chemical shift should arise from variations in Q_{4p}. An increase in the electron-withdrawing ability of the groups attached to selenium should increase Q_{4p} and so decrease the selenium shielding.[14] This conclusion is supported by the experimental data for a series of methyl derivatives in which the selenium shielding increases in the order: $MeSeO_2H$ [1] < $MeSeCl_3$ [2] < Me_2SeO [3] < Me_2SeCl_2 [9] < Me_2SeBr_2 [10] < Me_2Se_2 [16] < Me_3Se^+ [30] < Me_2Se [21] < MeSeH [25] < $MeSe^-$ [29].

This is the order of decreasing electronegativity of the groups attached to selenium, and a similar order is obtained when the more limited data available for other series of alkyl derivatives are considered.

The foregoing correlation applies when the overall range of effective electronegativity of the substituents of selenium is fairly large. However, when this is not so, as when the alkyl group is varied, the relationship breaks down. Thus in the alkyl derivatives R_2Se, R_2Se_2, RSeH, RSe^-, and R_2SeBr_2, the shielding effect of the group R increases in the order $Bu^t < Pr^i <$ Et < Me which is the opposite to that expected if the selenium chemical shift were dominated by the inductive effect of R. Similar behaviour of phosphorus shielding has been observed in the species R_3P, R_4P^+, and R_3PH^+, where it was found that the ^{31}P chemical shift is related

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to the amount of α-chain branching in the substituent.[15] Figure 1 shows that this effect is also given by the ^{77}Se chemical shifts and in fact the substituent parameters σ(Me) = 0, σ(Et) = −110, σ(Pr^i) = −220, σ(Bu^t) = −320, and σ(Ph) = −200, can be used to calculate the selenium chemical shift in R_2Se, RSeH, RSe^-, and R_2Se_2 by means of the additive relations (2)—(5) respectively.

$$\delta(R_2Se) = 108(\sigma_1 + \sigma_2) \qquad (2)$$

$$\delta(RSeH) = 139\sigma + 116 \qquad (3)$$

$$\delta(RSe^-) = 167\sigma + 332 \qquad (4)$$

$$\delta(R_2Se_2) = 67\sigma - 275 \qquad (5)$$

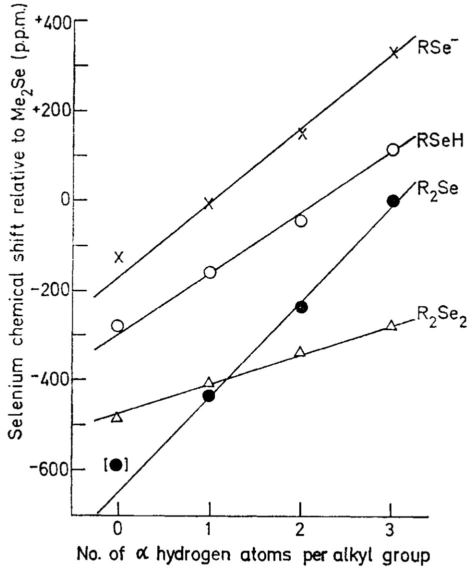

FIGURE 1 ^{77}Se Chemical shifts *vs.* number of α hydrogen atoms *per* alkyl group in alkyl selenide anions, selenols, selenides, and diselenides. The chemical shift of Bu^t_2Se ([●]) is an estimate based on the value for MeBu^{t}Se

These additive substituent parameters parallel those needed to predict phosphorus chemical shifts in tertiary phosphines, but are *ca.* eight times larger. The term Q_{4p} of equation (1) is proportional to the mean inverse volume occupied by the valence *p* electrons, $\langle r^{-3}_{4p(Se)} \rangle$, which has a value of 2·8 times $\langle r^{-3}_{3p(P)} \rangle$ which appears in the corresponding expression for ^{31}P chemical shifts, and this can account for the difference to some extent. However, it is difficult to attribute the remaining unexplained factor of almost three solely to a smaller value of Δ*E* in the selenium compounds, and it appears that the electron distribution at selenium is much more sensitive to changes in substituents than is that at phosphorus in similar compounds. This may be due to the greater polarisability of selenium, and a comparison with sulphur or arsenic shielding in analogous species would be of interest in this connection. It is noteworthy that the gradients of equations (2)—(5) increase as the effective electronegativity of the selenium decreases; that is as the selenium atom and the group R become of comparable electronegativity.

Most diselenides R_2Se_2 are coloured, and their relatively low-field selenium chemical shifts have been attributed[3] to small values of Δ*E*. Our data are consistent with this view, but it is also possible that the shift to lower field is due to an increase in Q_{4p} resulting from the higher electronegativity of the attached RSe group. Comparison of the data for Me_2Se_2 (16), Ph_2Se_2 (84), and PhSeSeMe (76) shows that replacement of a methyl group by phenyl deshields the neighbouring selenium nucleus by *ca.* 170 p.p.m., and the distant selenium nucleus by only *ca.* 17 p.p.m. That is, the contribution of the group RSe to the shielding of the other selenium nucleus in a diselenide is only slightly sensitive to the nature of R. The data for analogous biphosphines show that phosphorus shielding behaves similarly although the overall chemical shift range is much smaller (*e.g.* replacing methyl by phenyl deshields the attached phosphorus nucleus by only 22 p.p.m. in $R_2P{\cdot}PR'_2$).

Formation of a selenonium salt gives a large shift to low field. This is analogous to the change in phosphorus shielding that attends phosphonium salt formation; however, the change in selenium shielding depends both upon the nature of the added alkyl group and the groups already present. Thus the formation of Me_3Se^+ (30) from Me_2Se (21) is accompanied by a deshielding of 253 p.p.m., whereas when Me_2EtSe^+ (31) is formed from MeEtSe (20) the deshielding is only 183 p.p.m. Similarly the transformations Et_2Se (19) $\xrightarrow{EtI}$ $Et_3Se^+I^-$ (32) and Me_2Se (21) $\xrightarrow{EtI}$ $Me_2EtSe^+I^-$ (31) are accompanied by deshieldings of 144 and 291 p.p.m. respectively. It appears however that selenium chemical shifts in selenonium salts can be estimated from simple additivity relationships in analogy with the behaviour previously noted for phosphorus chemical shifts in quaternary phosphonium salts.[15] An important difference between these species is that in the latter the interbond angles at phosphorus are all close to the ideal tetrahedral angle of 109·5°, whereas in the selenonium ions the electron pair on selenium permits considerable variations in the interbond angles according to the bulk of the substituents.

The formation of a co-ordination compound by Me_2Se also gives a shift to low field (77), (78), but the magnitude of this change is only *ca.* half that observed on selenonium salt formation. This is analogous to the behaviour observed for phosphorus shielding in tertiary phosphines when these become co-ordinated.[16] It is difficult to rationalise the rather small difference in selenium chemical shift between the *cis*- and *trans*-isomers of $(Me_2Se)_2PtCl_2$ solely in terms of electron withdrawal

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[15] S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, 1967, **32**, 781; S. O. Grim and W. McFarlane, *Canad. J. Chem.*, 1968, **46**, 2071; S. O. Grim, W. McFarlane, E. F. Davidoff, and T. J. Marks, *J. Phys. Chem.*, 1966, **70**, 581.

[16] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 346.

from the Pt–Se bond as the electric field of the neighbouring chlorine atom(s) should also be taken into account. [See also the discussion of (80) and (81) later.]

In the *meta*- and *para*-substituted aryl methyl and ethyl selenides, ArMeSe and ArEtSe, there is a correlation between the ^{77}Se chemical shift and the Hammett σ constant for the aromatic substituent as shown in Figure 2. It is evident that increasing electron withdrawal from the selenium atom decreases the selenium shielding as would be expected for the reasons given earlier. There is evidence [17] that selenols can participate in hydrogen-bonding and this can affect the selenium shielding by more than 20 p.p.m. This probably accounts for the much poorer correlation observed for the substituted aryl selenols. The ^{77}Se chemical shifts of the *ortho*-substituted aryl methyl and ethyl selenides appear to be haphazard. The presence of a substituent in the position *ortho* to the selenium will reduce the tendency of the alkyl group to lie in the plane of the aromatic ring and so reduce the extent of interaction between the selenium lone pairs and the π-electron system of the ring.

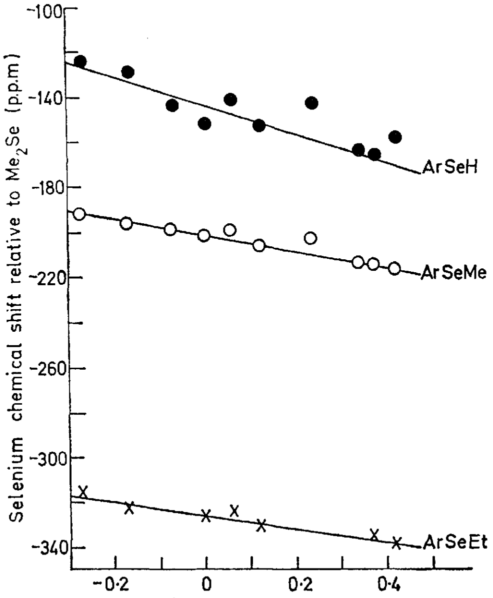
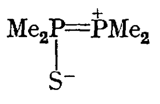


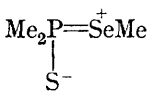
FIGURE 2 ^{77}Se Chemical shifts *vs.* Hammett σ constants in *meta* and *para* substituted aryl selenols and aryl methyl and ethyl selenides

The change in selenium shielding of 137 p.p.m. to lower field when a sulphur atom is attached to phosphorus in Me_2PSeMe (80) may be compared with a change in the phosphorus shielding of P^{III} of 2·5 p.p.m. to higher field which accompanies the formation of $Me_2P^{III}P(S)Me_2$ from $Me_2P{\cdot}PMe_2$.[18] Whilst structure (I) is likely to be important in the case of the biphosphine monosulphide the greater electronegativity of selenium will reduce the contribution of structure (II) in (81). The electric field due to the sulphur atom may also be important. Thus



$$\underset{\underset{S^-}{|}}{Me_2P}{=}\overset{+}{P}Me_2$$

(I)



$$\underset{\underset{S^-}{|}}{Me_2P}{=}\overset{+}{Se}Me$$

(II)

the decreased selenium shielding in (81) can be seen as a result of electron withdrawal by the sulphur atom, and the result for the phosphorus compounds can be regarded as anomalous by virtue of a contribution from (I).

The substantial deshielding observed in $(MeO)_2SeO$ (75) (in which the selenium atom has one lone pair of electrons) may be compared with the low-field ^{31}P shifts found in trialkyl phosphites. This is due to a large paramagnetic contribution resulting from a substantial *p*-electron imbalance in the three bonds to selenium or phosphorus.[19] In the quadruply connected selenates (73) and (74) this imbalance is somewhat redressed and the shielding is greater, as is also found with the trialkyl phosphates, $(RO)_3PO$.

The range of variation of coupling constants involving selenium is much less than in analogous phosphorus compounds. Thus for the transformation $P^{III} \rightarrow P^{V}$ a typical [20] change in $^2J(^{31}P \cdots H)$ is from $+2$ to -14 Hz, whereas the transformation $R_2Se \rightarrow R_3Se^+$ hardly affects $^2J(^{77}Se \cdots H)$. This may be because the selenium atom still has a lone pair of electrons in the cation and so the *s*-character of the hybrid orbitals forming the Se–C bonds need not alter much. $^3J(^{77}Se \cdots H)$ Is rather more sensitive to the oxidation state of selenium, and is exceptionally large (25 Hz) in dimethyl selenate (73). Of all the compounds examined here, this and the ethyl homologue are the only ones in which the selenium atom does not have a lone pair of electrons (the species R_2SeX_2 involve sp^3d selenium hybridisation) and so the *s*-character of the Se–OMe bonds is probably higher than in the other compounds. It is difficult to present a fuller discussion because it is likely that the magnitude of $^3J(^{77}Se \cdots H)$ depends upon the Se–O–C–H dihedral angle and so is affected by the conformer populations.

In the aryl selenols the coupling $^1J(^{77}Se{-}H)$ varies over a small range in an apparently haphazard manner, although it can be seen that the values are smallest in the *para*-substituted derivatives. However, there is a more systematic variation in the alkyl selenols RSeH (R = Me, Et, Pr^i, or Bu^t) again over a narrow range. This coupling constant is known to be positive,[5d] and its magnitude should increase with increasing electron withdrawal from the selenium atom.[21] Thus the observed trend is consistent with the normal inductive sequence for the alkyl groups. This is in marked contrast to the behaviour observed for the selenium shielding as discussed earlier.

In general, the trends of selenium chemical shifts are

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[17] W. McFarlane, to be published.

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[19] J. R. van Wazer, *Determ. Org. Struct. Phys. Meth.*, 1971, **4**, 323.

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similar to those found for phosphorus, although the overall range and sensitivity to changes in electronic environment are several times greater. These features should make ^{77}Se chemical shift measurements valuable for diagnostic purposes, especially when double-resonance facilities are available. The more limited range of variation of selenium coupling constants makes studies of these less attractive from this point of view.

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