# <sup>77</sup>Se N.m.r. Studies of Organoselenium Compounds

III—Substituent Effects in 4,4'-Disubstituted Diphenyl Selenides and 4,4'-Disubstituted Diphenylmethanes Studied by <sup>1</sup>H, <sup>13</sup>C and <sup>77</sup>Se Spectroscopy

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<sup>77</sup>Se N.m.r. spectra of 4,4'-disubstituted diphenyl selenides have been obtained. The chemical shifts could be correlated with substituent constants of the Hammett type or with Swain and Lupton two-parameter equations. No correlations were observed between these <sup>77</sup>Se shifts and the <sup>13</sup>C shifts of the CH<sub>2</sub> group of 4,4'-disubstituted diphenylmethanes, the latter shifts showing no correlation with substituent constants. On the other hand linear correlation was observed between the <sup>77</sup>Se shifts of the 4,4'-disubstituted diphenyl selenides and the <sup>1</sup>H shifts of the CH<sub>2</sub> group of the diphenylmethanes, the <sup>13</sup>C shifts of their 1-carbons and the <sup>19</sup>F shifts of 4-substituted fluorobenzenes.

# **INTRODUCTION**

In our previous work, the effect of substituents on the  $\frac{77}{8}$  and  $\frac{1}{2}$  and <sup>7</sup>Se n.m.r. chemical shifts in 2- and 3-substituted selenophenes<sup>1</sup> were studied by the Fourier transform technique. We also investigated the 77Se shifts of a large number of arylmethylseleno-substituted alkanoic acids.<sup>2</sup> We were therefore interested in using the <sup>77</sup>Se shifts of 4,4'-disubstituted diphenyl selenides as a probe for the interaction between the substituents and the selenium atom. In this paper, a representative set of 4,4'-disubstituted diphenyl selenides, containing strongly electron donating and strongly electron attracting substituents, as well as substituents of intermediate character such as methyl and the halogens. has been studied. Systematic studies of the <sup>77</sup>Se n.m.r. spectra of this class of compounds have not previously been undertaken, although the spectrum of diphenyl selenide has been recorded.<sup>3</sup> McFarlane<sup>4</sup> has reported the double resonance spectra (INDOR) of some 4substituted phenylmethyl selenides, phenylethyl

selenides, and of some 4-substituted phenyl selenols. In our previous studies of the <sup>13</sup>C, <sup>1</sup>H and <sup>77</sup>Se shifts of monosubstituted selenophenes, <sup>1,5</sup> we were able to draw some interesting conclusions about the relative sensitivity of similarly situated <sup>13</sup>C and <sup>77</sup>Se nuclei to substituent effects. The <sup>77</sup>Se shifts appeared to be approximately six times more sensitive. In order to make similar comparisons possible in the case of diaryl selenides, we have synthesized a series of 4,4'disubstituent-caused <sup>1</sup>H and <sup>13</sup>C shifts of the methylene group and the <sup>13</sup>C shifts of the 4 ring carbons.

#### **RESULTS AND DISCUSSION**

The n.m.r. parameters of the above-mentioned compounds are collected in Tables 1 and 2. It is obvious from inspection of these tables that while the selenium shifts vary in a regular way with the character of the substituents, electron donating groups causing large upfield shifts and electron attracting large downfield shifts, the effect of substituents on the <sup>13</sup>C shifts of the

Table	1.	<sup>77</sup> Se n.m.r. chemical shifts of 4,4'-
		disubstituted diphenyl selenides in
		dimethyl sulphoxide/chloroform
		(50:50) solution at 19.135 MHz
		relative to the <sup>77</sup> Se absorption
		of selenophene and the unsub-
		stituted diphenyl selenide

Substituent	δ <sup>77</sup> Se (ppm)	δΔ <sup>77</sup> Se (ppm)
н	-193.1	0
NH <sub>2</sub>	-231.3	-38.2
OCH₃	-221.1	-28.0
OC <sub>6</sub> H <sub>5</sub>	-214.8	-21.7
SCH₃	-204.6	-11.5
F	-203.8	-10.7
CI	-196.8	-3.7
Br	-200.2	-7.1
1	-206.4	-13.3
CH₃	-209.3	-16.2
CO₂H	-180.0	+13.1
COCH₃	-178.7	+14.4
NO₂	-169.3	+23.8

 $\Delta \delta^{77}$ Se =  $\delta^{77}$ Se (substrate)- $\delta^{77}$ Se (reference); positive values are downfield.

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Table 2.13C and 1H n.m.r. chemical shifts of the methylene<br/>group and C-1 in 4,4'-disubstituted diphenyl-<br/>methanes in hexadeuterioacetone solution, at<br/>15.0 MHz and 100 MHz respectively, relative to<br/>TMS and the unsubstituted diphenylmethane\*

Substituent	δ <sup>13</sup> C (ppm) —CH <sub>2</sub> —	Δδ <sup>13</sup> C (ppm) CH <sub>2</sub>	δ <sup>13</sup> C (ppm) C-1	Δδ <sup>13</sup> C (ppm) C-1	δ <sup>1</sup> H (ppm) CH <sub>2</sub>	Δδ <sup>1</sup> Η (ppm) —CH <sub>2</sub> —
н	42.37	0	142.24	0	3.931	0
NH <sub>2</sub>	40.82	-1.55	131.10	-11.14	3.716	-0.215
OCH₃	40.67	-1.70	133.60	-8.64	3.820	-0.111
ОН	40.66	-1.71	133.52	-8.72	3.738	-0.193
SCH₃	41.15	-1.22	139.03	-3.21	3.837	-0.094
F	40.42	-1.95	136.44	-5.80	3.876	-0.055
CI	40.74	1.63	140.37	-1.67	3.869	-0.062
Br	40.82	-1.55	140.90	-1.34	3.818	-0.113
I	41.07	1.30	141.50	-0.74	3.812	-0.119
CH₃	41.56	-0.81	139.36	-2.88	3.857	0.074
COCH <sub>3</sub>	41.96	-0.41	145.56	+3.32	4.068	+0.137
NO <sub>2</sub>	41.56	-0.81	148.69	+6.45	4.237	+0.300

<sup>a</sup>  $\Delta \delta^{13}C$  as well as  $\Delta \delta^{1}H = \delta$  (substrate) –  $\delta$  (reference); positive values are downfield.

CH<sub>2</sub> group of diphenylmethanes is small and always upfield. There is no linear correlation between the <sup>77</sup>Se shifts of the diphenyl selenides and the <sup>13</sup>C shifts of the CH<sub>2</sub> group of the diphenylmethanes. However, linear correlations are found to exist between the <sup>77</sup>Se shifts and the <sup>1</sup>H proton shifts (r=0.92) of the CH<sub>2</sub> protons, and the <sup>13</sup>C shifts of the 1-carbon in the diphenylmethanes (r=0.95). Excellent correlations (r=0.97) were also found between the <sup>77</sup>Se shifts and the <sup>19</sup>F shifts of 4-substituted fluorobenzenes taken from the literature<sup>6</sup> (Fig. 1).

A large number of different types of substituent parameters obtained from reactivity data are available.<sup>7</sup> A very good linear correlation was obtained when the <sup>77</sup>Se shifts of the diphenyl selenides were plotted against the  $\sigma_p^+$  values of Swain and Lupton<sup>8</sup> (r = 0.98). Correlation with the classical Hammett<sup>7</sup>  $\sigma_p$ values was, however, almost as good, while with Brown and Okamoto's  $\sigma_p^+$  values<sup>9</sup> the correlation coefficient was somewhat lower (cf. Table 3). McFarlane<sup>4</sup> observed correlations with Hammett's  $\sigma_p$  values for the limited number of 4-substituted phenyl selenols, phenylmethyl selenides, and phenylethyl selenides which he studied.



Figure 1. Correlation of the  $\Delta \delta^{77}$ Se chemical shifts of 4,4'disubstituted diphenyl selenides with the  $\Delta \delta^{19}$ F of 4-substituted fluorobenzenes.<sup>6</sup>  $\Delta \delta^{77}$ Se = 2.47  $\Delta \delta^{19}$ F -0.44 (r = 0.97).

Applying the two-parameter equation of Swain-Lupton<sup>8</sup> did not improve the correlation, although it should give an indication of the contribution of the mesomeric and inductive effects to the substituentcaused shift (cf. Table 3). The 1-carbon and the CH<sub>2</sub> protons of the diphenylmethanes and the <sup>19</sup>F shifts of the 4-substituted fluorobenzenes also gave correlations with the Swain and Lupton parameters (cf. Table 3). The only good correlation found for the <sup>13</sup>C shift of the methylene group of diphenylmethane was for the four halo derivatives, which showed a good correlation (r = 0.97) with the electronegativity (according to Pauling):  $\Delta \delta = -0.40E_x - 0.37$ . It is interesting to note that the 4,4'-halodiphenyl selenides did not show such a correlation. From the correlations between the <sup>19</sup>F shifts of 4-substituted fluorobenzenes<sup>6</sup> and the <sup>77</sup>Se shifts of 4,4'-disubstituted diphenyl selenides (Fig. 1), it can be seen that the <sup>77</sup>Se shifts are approximately 2.5 times more sensitive than the <sup>19</sup>F shifts, and from the Swain and Lupton equations it seems that the <sup>77</sup>Se and <sup>19</sup>F shifts are affected in the same way by inductive and mesomeric effects. (Table 3).

Our results might indicate that a nucleus bound to a benzene ring gives a correlation with the substituent constants of substituents in the 4-position if the atom in question has a free electron-pair. We have only found a few 4-substituted triarylphosphines in the literature,<sup>10,11</sup> but their shifts do not contradict this

 Table 3. Equations for the correlations of the shifts in Tables 1 and 2 with different types of reactivity parameters

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Set of reactivity parameters	Equation	r°	<sub>0</sub> ط
$\sigma_{\mathbf{p}}^+$ of Swain and Lupton	$\Delta \delta^{77} Se = 33.3 \sigma_{p}^{+} - 5.41$	0.98	
$\sigma_{p}$ of Hammett	$\Delta \delta^{77} Se = 43.7 \sigma_p - 12.91$	0.97	
$\sigma_p^+$ of Brown and Okamoto	$\Delta \delta^{77} Se = 27.25 \sigma_{p}^{+} - 5.47$	0.93	
F and R of Swain and Lupton	$\Delta \delta^{77}$ Se = 6.77 + 16.42 $\mathscr{F}$ + 53.31 $\mathscr{R}^{a}$	0.98	3.86
${\mathcal F}$ and ${\mathcal R}$ of Swain and Lupton	$\Delta \delta^{13}$ C-1 = 0.74 + 3.06 $\mathscr{F}$ + 16.87 $\Re^{a}$	0.98	1.09
${\mathscr F}$ and ${\mathscr R}$ of Swain and Lupton	$\Delta \delta^{1} H(CH_{2}) = -0.023 + 0.118 \mathcal{F} + 0.387 \mathcal{R}^{a}$	0.81	0.088
${\mathscr F}$ and ${\mathscr R}$ of Swain and Lupton	$\Delta \delta^{19} \dot{F}^{b} = 1.35 + 4.74 \mathscr{F} + 22.74 \Re^{a}$	0.98	1.44

<sup>&</sup>lt;sup>a</sup> Ten common substituents: NH<sub>2</sub>, OCH<sub>3</sub>, SCH<sub>3</sub>, F, Cl, Br, I, CH<sub>3</sub>, COCH<sub>3</sub>, and NO<sub>2</sub>.

<sup>b</sup> 4-Substituted fluorobenzenes.

<sup>c</sup> Correlation coefficient.

<sup>d</sup> Standard deviation in ppm.

proposal. An extended study of the <sup>31</sup>P shifts of such compounds and of benzylic carbanions would be of interest in this connection.

### **EXPERIMENTAL**

#### N.m.r. Spectra

The <sup>77</sup>Se n.m.r. spectra were obtained at 19.135 MHz on a Varian XL-100-15 spectrometer equipped with frequency sweep, proton wide band decoupler and Fourier transform operation. Field-frequency control (lock) was effected by means of the deuterium resonance of hexadeuterioacetone. Computer-controlled time averaging of 15 000-20 000 transients was used. The shifts were determined with an accuracy of  $\pm 0.2$  ppm relative to an external selenophene standard, consisting of a 20% solution of selenophene in deuterioacetone in a 12 mm tube surrounding a 10 mm tube containing a saturated solution of the sample in dimethyl sulphoxide and chloroform (50:50). The resulting film between the two tubes enabled the use of deuterium as the internal lock signal and  $7^7$ Se in selenophene as the external reference. The region for the  $7^7$ Se absorption of the diaryl selenides was 200 ppm upfield from the <sup>77</sup>Se absorption in selenophene. The <sup>77</sup>Se chemical shifts were determined from the proton-decoupled spectra. The <sup>13</sup>C n.m.r. spectra were obtained at 15.0 MHz with a JEOL JNM-60 spectrometer with a built-in JEOL 980 A computer with 12 K memory, and the <sup>13</sup>C chemical shifts were determined from proton-decoupled spectra. The <sup>1</sup>H n.m.r. spectra were obtained with a JEOL MH 100 high resolution spectrometer. Deuterioacetone was used as a solvent in the <sup>13</sup>C as well as the <sup>1</sup>H n.m.r. measurements of the 4,4'disubstituted diphenylmethanes, because it enabled us to use deuterium as the internal lock signal for <sup>13</sup>C measurements. 4,4'-Dicarboxydiphenylmethane was the only compound neither soluble in deuterioacetone nor in the dimethyl sulphoxide/chloroform mixture. The i.r. spectra were recorded on a Perkin-Elmer Model 257 instrument. The gas chromatographs used were a Perkin-Elmer 900 analytical instrument and a Perkin-Elmer F 21 preparative instrument. Mass spectra were obtained with an LKB 9000 mass spectrometer. Elementary analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr.

### Compounds

Most of the 4,4'-disubstituted diphenyl selenides and diphenylmethanes used in this study are known, and their melting points, yields and references to procedures for their preparation are given in Tables 4 and 5. The purity and structures of the compounds were checked by gas chromatography, i.r., <sup>1</sup>H n.m.r. and mass spectroscopic analysis.

Some of the compounds were, however, unknown or prepared by modified procedures. These syntheses are presented below.

Table 4. Melting or boiling points, yields and references for the preparation of the 4,4'-disubstituted diphenyl selenides

R	M.p. or b.p. °C	M.p. or b.p. lit. ℃	Yield %	Yield lit. %	Ref.
н	166-168/12	300-315/760	68	79 <b>–8</b> 6	12
NH <sub>2</sub>	112-114	115	72	85–90	13
OCH <sub>3</sub>	5657	56.5-58	10	11	14
OC <sub>6</sub> H <sub>5</sub>	80-83	83-85	56	62	15
SCH <sub>3</sub>	5254		52	_	*
F	151-154/12		24	_	16
CI	9496	96	57		17
Br	112-113	114.0-114.8	53	_	18
1	101–113		56	—	a
CH₃	68.569	69.5	57		29
COCH <sub>3</sub>	90-91	91–92	66	70	19
CO₂H	318-321	320	53		20
NO2	174-175	172–173	76	80	21

\* For preparation, see 'Experimental.'

4,4'-Dimethylthiodiphenyl selenide. 19.5 ml of 1.13 N n-butyllithium in hexane were added dropwise to a solution of 3.9 g (0.01 mol) of 4,4'-dibromodiphenyl selenide in 150 ml of dry ether with stirring under nitrogen at room temperature. When the addition was complete, the reaction mixture was refluxed for 30 min. After cooling to room temperature, 2.20 g (0.022 mol) of dimethyl disulphide in 10 ml of dry ether were added dropwise with stirring. After stirring for two h, the brown precipitate was filtered off and dissolved in boiling chloroform. After hot filtration and drying over magnesium sulphate, the chloroform solution was concentrated. The residue was recrystallized from 95% ethanol, yielding 1.7 g (52%) of light brown crystals, m.p. 52-54 °C. In the mass spectrum, the peaks due to the molecular ion centred at m/e 326 showed the same pattern as the spectrum simulated for one selenium and two sulphur atoms. The base peak is due to  $(M-Se)^+$ . (Found: C 52.67; H 4.43. Calc. for  $C_{14}H_{14}S_2Se: C 51.68; H 4.34$ ).

p-Iodophenyldiazonium tetrafluoroborate. At  $80 \,^{\circ}C$ , 8.8 g (0.40 mol) of p-iodoaniline were suspended in a

 
 Table 5. Melting points, yields and references for the preparation of the 4,4'-disubstituted diphenylmethanes

_	М.р.	M.p.	Yield	Yield lit. %	Ref.
R	°C	lit. °C	%		a
Н		23–26			
NH <sub>2</sub>	92–93	92-93	62	60–70	22,23
OCH₃	5051	5152	67	79	24
он	157–159	158	87	~100	25
SCH₃	60-62	63.5-64	65	83	26
F	2325	27.0-27.4	48		27
CI	54-56	55-56	44	50	28
Br	6364	64	62	70	29
1	89-91	9293	6	4	30
CH₃	24–27	22.5	71		31 <sup>b</sup>
COCH <sub>3</sub>	91–92	92.5-93	27	34	32
CO₂H	317-319	322323	65		33 <sup>ь</sup>
NO2	186–188	187	32	26	25,34

<sup>a</sup> Purchased from B.D.H. Laboratory Chemicals Division, Poole, England.

<sup>b</sup> For preparation, see 'Experimental.'

mixture of 100 ml of water and 10 ml of conc. hydrochloric acid. The suspension was cooled to 0 °C and treated with a solution of 2.8 g (0.041 mol) of sodium nitrite in 15 ml of water. The temperature was maintained at 0 °C by the addition of crushed ice. When the diazotization was complete, the stirring was continued for an additional 10 min, whereupon the reaction mixture was filtered and the filtrate treated dropwise at -5 to 0 °C with 40 ml (0.055 mol) of 10% hydrogen tetrafluoroborate. After stirring the reaction mixture at 0 °C for another 45 min, the precipitate was filtered off, washed with cold water and air dried. 8.9 g (69%)of orange-yellow crystals were obtained, which decomposed with evolution of nitrogen at 119 °C. The  $-N^+ \equiv N$  i.r. absorption appeared at 2255 cm<sup>-</sup>

4,4'-Diiododiphenyl selenide. A solution of sodium hydrogen selenide was prepared according to Ref. 35 from 1.2 g (0.015 mol) of black selenium and 1.25 g (0.033 mol) of sodium borohydride. To this solution, 8.9 g (0.028 mol) of p-iodophenyl diazonium tetrafluoroborate were added in portions with vigorous stirring, whereupon a brown precipitate was immediately formed. After stirring the reaction mixture for another h, the precipitate was filtered off and dissolved in chloroform. The filtrate was extracted twice with chloroform and the combined phases were dried over magnesium sulphate. The chloroform was evaporated and the residue recrystallized from ethanol/water, giving 3.8 g (56%) of crude product, m.p. 86-98 °C. The product was purified by sublimation in vacuum, giving 2.5 g of orange-yellow crystals, m.p. 101-113 °C.

In the mass spectrum, the peaks centred at m/e 486  $(M^+ \text{ and base peak})$  and 359  $(M^+ - I)$  show the same patterns as a spectrum simulated for one selenium atom. (Found: C 29.70; H 1.59; Se 16.60. Calc. for C<sub>12</sub>H<sub>8</sub>I<sub>2</sub>Se: C 29.72; H 1.66; Se 16.28.)

4,4'-Dicarboxydiphenyl selenide. 19.5 ml of 1.13 N *n*-butyllithium in hexane were added dropwise with stirring under nitrogen at room temperature to 3.9 g (0.01 mol) of 4,4'-dibromodiphenyl selenide in 150 ml dry ether. When the addition was complete, the reaction mixture was refluxed for 30 min, whereupon it was poured on to crushed carbon dioxide covered with dry ether. At 0 °C the reaction mixture was treated with 300 ml of water, the water phase was separated

and the ether phase extracted with 5 N sodium hydroxide solution. The combined aqueous phases were acidified with 2 N hydrochloric acid to pH=2. The precipitate was filtered off and recrystallized from acetic acid, yielding 1.7 g (53%) of the product, m.p. 318-321 °C; Lit.<sup>19</sup> m.p. 321-323 °C.

4,4'-Dimethyldiphenylmethane. To a solution of 8.2 g (0.025 mol) of 4,4'-dibromodiphenylmethane in 100 ml of dry ether, 46 ml of 1.25 N butyllithium in hexane were added dropwise with stirring under nitrogen at room temperature. When the addition was complete, the reaction mixture was refluxed for 30 min, and then cooled in an ice-bath to 5 °C. 7.2 g (0.057 mol) of dimethyl sulphate in 50 ml of dry ether were added to the reaction mixture at such a rate that a gentle reflux was maintained. After stirring for an additional 15 min, the excess of dimethyl sulphate was hydrolyzed with 50 ml of conc. ammonia and stirring was continued for 1.5 h. The organic phase was separated, washed with water until neutral, dried over magnesium sulphate and evaporated. Upon standing in a refrigerator, 3.5 g (71%) of colourless crystals, m.p. 24–27 °C, was obtained; Lit.<sup>30</sup> m.p. 22.5 °C.

4,4'-Dicarboxydiphenylmethane. To a solution of 8.2 g (0.025 mol) of 4.4'-dibromodiphenylmethane in 100 ml of dry ether, 46 ml of 1.25 N butyllithium in hexane were added dropwise with stirring under nitrogen at room temperature. When the addition was complete, the reaction mixture was refluxed for 30 min, whereupon it was poured on to crushed carbon dioxide covered with dry ether. At 0 °C the reaction mixture was treated with 250 ml of water, the water phase was separated and the ether phase extracted with 5 N sodium hydroxide solution. The combined aqueous phases were acidified with 2 N hydrochloric acid to pH 2. The precipitate was filtered off and recrystallized from acetic acid, yielding 3.2 g (65%) of the product, m.p. 317-319 °C; Lit.<sup>3</sup> m.p. 322-323 °C.

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