June, 1983] © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 1651—1664 (1983) 1661

Studies on Long-range Couplings between ^{77}Se and ^{13}C in Some Aryl Selenides, Dichlorides, and Selenoxides. The Inverse Effect on Couplings in the Selenoxide Formation

Warō NAKANISHI* and Yoshitsugu IKEDA
Department of Chemistry, Faculty of Education, Wakayama University, Masagocho, Wakayama 640

(Received September 20, 1983)

Long-range coupling constants between ^{77}Se and ^{13}C in selenoanisole, diphenyl selenide, diphenyl diselenide, and their 2-mono- and 2,2′-disubstituted derivatives, selenoxanthone, selenanthrene, dichlorides, and selenoxides were measured to disclose predominant factors governing the magnitude of the coupling. Extraordinary large values for two- and three-bond couplings are found in selenoxanthone. Three factors are operative: the orientational effect, the coordination number, and the effect of ring formation. The last factor accompanies a stronger inverse effect on the coupling of selenoxides than on that of selenides.

Since selenium has a magnetic isotope ^{77}Se with nuclear spin 1/2 and natural abundance 7.6%, one can study the structure and reactions of organoselenium compounds directly by NMR spectroscopy.[1–4] Chemical shifts have been shown to be correlated with the oxidation state of selenium atom.[1,2] Coupling constants appear to reflect the stereochemistry of organoselenium compounds.[1,2,4] Reich and Trend,[4] for example, have shown a stereochemical dependence of geminal ^{77}Se–^{13}C spin coupling constants in sterically fixed three-coordinated selenium compounds, *i.e.*, a selenonium salt, a selenoxide, and an ylide. In each case, one methyl carbon atom *cis* to the lone pair is substantially more strongly coupled than the other two.

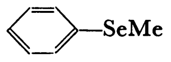
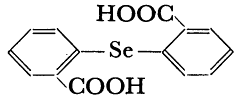
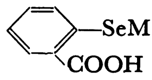
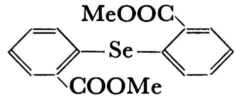
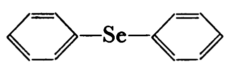
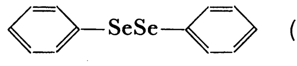
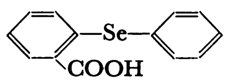
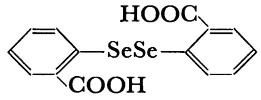
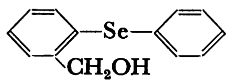
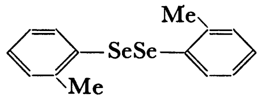
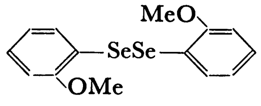
We wish to report here long-range couplings in some aromatic organoselenium compounds which show interesting structural correlations.

Results and Discussion

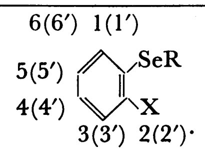
Orientational Effect of the Lone Pair(s). The two- and three-bond coupling constants between ^{77}Se and ^{13}C (^2J(Se–C) and ^3J(Se–C), respectively) of selenoanisole (**1**), diphenyl selenide (**2**), diphenyl diselenide (**3**), their 2-mono- and 2,2′-disubstituted derivatives, selenoxanthone (**4**), and selenanthrene (**5**) were measured[5] and the results are shown in Tables 1 and 2.

The ^2J(Se–C(2,6)) values of **1**, **2**, and **3** are all about 11 Hz. The ^2J(Se–C(2′,6′)) values of 2-(phenylseleno)benzoic acid and 2-(hydroxymethyl)phenyl phenyl selenide are 11.1±0.7 Hz, but the ^2J(Se–C(6)) values of these compounds are 6.0±0.5 Hz. Then the ^2J(Se–C) values between selenium and *ortho*-carbon of the benzene ring which has no additional substituent are about 11 Hz, and those associated with substituent attachment

TABLE 1. TWO-BOND COUPLINGS BETWEEN ^{77}Se AND ^{13}C OF SOME ORGANOSELENIUM COMPOUNDS[a)]

Compound[b)]	^2J(Se–C(6))	^2J(Se–C(2′,6′))	Compound[b)]	^2J(Se–C(2,2′))	^2J(Se–C(6,6′))
 (**1**)	11.0	—		c	<3
	6.6	—		c	<3
 (**2**)	11.0	11.0	 (**3**)	11.0	11.0
	6.4	10.4		c	4.4
	5.5	11.8		12.8	3.4
				13.7	4.6

a) In Hz. b) Numbers are assigned as follows:



c) Difficult to measure because of low solubility or low sensitivity.

Table 2. ^{13}C NMR chemical shifts and coupling constants of **4**, **5**, **11**, and **12**

Compd	Chemical shift[a]							Coupling constant[b]		
	C(1,1′)	C(2,2′)	C(3,3′)	C(4,4′)	C(5,5′)	C(6,6′)	C=O	^2J(Se–C(6,6′))	^3J(Se–C(5,5′))	^3J(Se–C(3,3′))
4	134.9	130.8	131.2	126.6	132.0	128.1	181.7	34.0	11.9	2.7
11	142.4	130.8	130.3	132.1	134.1	129.5	182.0	22.9	4.7	
5	134.4	134.4	131.1	127.9	127.9	131.1		24.0	6.5	
12	144.7	144.7	128.5	131.2	131.2	128.5		19.0	<3	

a) In ppm from TMS in CDCl$_3$. b) In Hz.

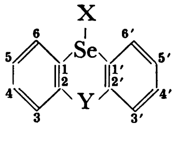
at the other *ortho*-position are about 6 Hz in these five compounds. These results suggest that ^2J(Se–C) values are small when the steric repulsion between the substituent at the *ortho*-position of a benzene ring and the group attached to the selenium increases the population of the group at the selenium in the neighborhood of the carbon of benzene ring carrying the substituent at the other *ortho*-position, *i.e.*, they are small when the lone pair of electrons is on the average far from the carbon under consideration.

This is further confirmed by an examination on ^2J(Se–C) in 2,2′-disubstituted diphenyl selenides and diphenyl diselenides. The ^2J(Se–C(6,6′)) values of 2,2′-diselenodibenzoic acid, di-2-tolyl and bis(2-methoxyphenyl) diselenides are 3.4—4.6 Hz and not affected by electronic properties of the substituents. Those for 2,2′-selenodibenzoic acid and its dimethyl ester are too small to measure. The ^2J(Se–C(2,2′)) values of di-2-tolyl and bis(2-methoxyphenyl) diselenides are 12.8 and 13.7 Hz, respectively, and are larger than that of diphenyl selenide.

When the selenium atom retains at least one lone pair of electrons, the 4s-atomic orbital of selenium to be used for bonding is expected to be low.[6] Namely, most of the s-character of selenium in organoselenium compounds is attributable to its lone pair(s). Since indirect nuclear-nuclear spin couplings are mainly governed by the Fermi contact term[7] and therefore by the s-overlap integral of the bonds under consideration, the orientation of the lone pair of electrons on the selenium atom is important.

Examination of the ^2J(Se–C) values of **4** and **5** is necessary to clarify the effect of the orientation of lone pair of electrons because the ^2J(Se–C(6,6′)) values of **4** and **5**[8] are expected to be larger since the lone pairs of these compounds should spread over carbons C(6) and C(6′). Table 2 shows NMR data for **4** and **5**. Actually, very large ^2J(Se–C) values have been obtained for **4** and **5**, which are 34.0 and 24.0 Hz, respectively. Especially, the ^2J(Se–C) value of **4** is the largest that has ever been obtained for selenides to the best of our knowledge, which is almost the same as that reported for certain ylides.[4] These results provide support for the importance of the orientation of lone pairs for ^2J(Se–C). Three-bond couplings, ^3J(Se–C), were also found in **4** and **5**. The value of ^3J(Se–C(5,5′)) is larger than that of ^3J(Se–C(3,3′)) in **4** and the former is also larger than that of ^3J(Se–C(5,5′ or 4,4′)) of **5**.

The large couplings of selenium with C(6) and C(5) in **4** indicate effective spread of lone pairs over these carbons. The carbonyl group has a smaller covalent radius than selenium, which renders a favorable space to the lone pair of electrons to interact with these carbons, and since the group is likely to arrange the two benzene rings coplanar due to its sp^2 hybridization state, the selenium can interact with the carbons advantageously. That the value of ^3J(Se–C(3,3′)) is smaller than that of ^3J(Se–C(5,5′)) may also indicate the orientational effect of lone pairs.



	X	Y
4	None	C=O
5	None	Se
11	O	C=O
12	O	Se=O

The large ^2J(Se–C) and ^3J(Se–C) values in **5** may also be explained in terms of the effective spread of lone pairs over these carbons.

After all, these couplings may be well understood on the basis of the orientation of the lone pair of electrons on the selenium.

Effect of the Coordination Number. As ^2J(Se–C) is essentially related to the s-character of selenium and carbon atoms in the bonds,[7] it is expected to vary with change in the coordination number of the selenium atom. Table 3 shows ^{13}C NMR chemical shifts and coupling constants, ^2J(Se–C) and ^3J(Se–C), of **1**, **2**, dichlorides **6** and **7**, selenoxides **8** and **9**, and diphenyl selenone (**10**). The values of ^2J(Se–C) become larger in the order: selenides, dichlorides, and selenoxides. The chemical shift of the C(2) carbons of these organoselenium compounds as well as some aromatic organosulfur compounds[9] moves to higher field if the substituent is electronegative; that is, the ^2J(Se–C) values should be related to the electron-withdrawing ability of the selenium atom and therefore are related to the ^{13}C chemical shift of the C(2) carbons. As shown in Fig. 1, the plots of ^2J(Se–C) value *vs.* ^{13}C chemical shift show a trend in which the slope for the selenoanisoles is more

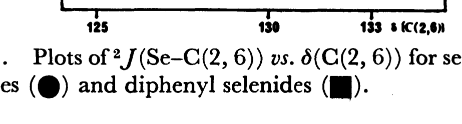


Fig. 1. Plots of ^2J(Se–C(2, 6)) *vs.* δ(C(2, 6)) for selenoanisoles (●) and diphenyl selenides (■).

Table 3. ^{13}C NMR chemical shifts and coupling constants of selenoanisoles and diphenyl selenides

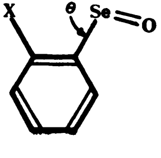
Compound	Chemical shift$^{a)}$					Coupling constant$^{b)}$	
	C(1)	C(2,6)	C(3,5)	C(4)	C(Me)	^2J(Se–C(2,6))	^3J(Se–C(3,5))
PhSeMe (**1**)	131.7	130.2	128.8	125.9	7.2	11.0	
$PhSeCl_2Me$ (**6**)	141.0	128.5	129.9	131.7	45.7	13.2	
PhSe(O)Me (**8**)	139.6	126.0	129.9	131.6	36.1	15.4	
PhSePh (**2**)	131.0	132.8	129.2	127.2		11.0	
$PhSeCl_2Ph$ (**7**)	142.4	131.2	129.7	131.6		11.2	
PhSe(O)Ph (**9**)	142.7	126.1	129.6	131.2		15.4	
$PhSeO_2Ph$ (**10**)	142.4	126.8	130.2	134.0		13.9	14.6

a) In ppm from TMS in $CDCl_3$. b) In Hz.

negative than that for the diphenyl selenides. Since the sign of ^2J(Se–C) is expected to be positive except **10** with which a negative sign is expected,[6] **10** should be put aside from the plots.

An unexpectedly large ^3J(Se–C) value (14.6 Hz) was found for **10**. This may be due to the increased s-character of the bonds caused by the lack of lone pair of electrons which carry otherwise most of the s-character of the selenium atom.[6]

Effect of the Ring Formation—The Inverse Effect on the Long-range Couplings. The ^{13}C NMR chemical shifts and the long-range coupling constants, ^2J(Se–C) and ^3J(Se–C), of selenoxanthone 10-oxide (**11**) and selenanthrene 9,10-dioxide (**12**) are collected in Table 2. Although the selenoxide formation from **1** and **2** to **8** and **9** increases the ^2J(Se–C) values of these compounds, the values for **11** and **12** are 22.9 and 19.0 Hz, respectively, which are smaller than those for **4** and **5**. The decrease in the long-range couplings between selenium and carbon with the formation of selenoxides relative to that of selenides (the inverse effect) is also found in the three-bond couplings, ^3J(Se–C), of **11** and **12** relative to those of **4** and **5**. The inverse effect may be attributed to the cyclic structure of **11** and **12**. Since ^2J(Se–C) values of **11** and **12** are still larger than those of **8** and **9**, the oxygens in **11** and **12** are supposed to operate in a way to increase the coupling constant but they could not overcome the disadvantageous steric factor. In other words, the s-orbital of the selenium atoms of **11** and **12** could not interact with that of the carbons in the benzene rings so effectively as in **4** and **5**. As mentioned above, the ^2J(Se–C) value of **4** is extraordinary large, which is three times as large as that of **2**, and the value of **5** is twice as large as that of **2**. Then the inverse effect on the long-range coupling in these compounds may be caused by the extraordinary large values resulting from the cyclic structure of these compounds. If the main factor for determining the large coupling constants is the sp^2-character of the selenium atoms in **4** and **5**, the factor should be smaller in **11** and **12** because the formation of selenoxides is expected to increase the sp^3-character of selenium atom. The increased sp^3-character may also decrease the values of ^3J(Se–C) of **11** and **12**. The increase in sp^2-character in **4** and **5** must be due to the cyclic structure with selenium atom(s) in the ring where the steric strain results in change in bond angle.



Experimental

^{13}C NMR spectra were obtained on a JEOL FX-60Q spectrometer operating at 15 MHz using chloroform as the solvent and tetramethylsilane as the internal standard. Spectral widths of 600, 1000, 3000, and 3500 Hz with 8 K data points and 30° or smaller pulses were employed. ^{77}Se–^{13}C coupling constants were obtained by observing the ^{77}Se satellites in ^{13}C spectra. A selective decoupling mode was also applied to assignment of ^{13}C chemical shifts if conditions were favorable.

Materials. The following compounds were prepared as described in the literature: 2-(methylseleno)benzoic acid,[10] 2-(phenylseleno)benzoic acid,[11] 2,2′-selenodibenzoic acid[12] and its dimethyl ester,[13] 2,2′-diselenodibenzoic acid,[10] selenoxanthone (**4**)[12] and its 10-oxide (**11**),[12] and selenanthrene 9,10-dioxide (**12**).[14] Physical properties agreed well with those in the literature.

Bis(2-methoxyphenyl) Diselenide. 2-Methoxyselenophenol, which had been prepared from 2-methoxyphenylmagnesium bromide and selenium in ether,[15] was oxidized in hexane with air. Recrystallization from hexane gave the diselenide in good yield, yellow needles, mp 85—87 °C. Found: C, 45.19; H, 3.72%. Calcd for $C_{14}H_{14}O_2Se_2$: C, 45.16; H, 3.76%.

Di-2-tolyl Diselenide. This compound was prepared as above in a red oil. Found: C, 49.82; H, 4.38%. Calcd for $C_{14}H_{14}Se_2$: C, 49.43; H, 4.15%.

Selenanthrene (5). To an ethanol solution (150 ml) of sodium diselenide, which had been prepared from selenium (12 g), sodium borohydride (3.2 g), and sodium hydroxide (3.0 g) according to the methods of Klayman and Griffin[16] and Bogert and Stull,[17] was added a solution of 2-chloronitrobenzene (19.5 g) in 50 ml of ethanol and refluxed for 3 h. After work-up, crystallization from acetic acid gave 2,2′-dinitrodiphenyl diselenide, yellow needles, 10.7 g (43%), mp 209—210 °C (lit,[17] 209 °C).

The diselenide (10.7 g) was dissolved in 30% aqueous dioxane (150 ml) and treated with hydrochloric acid and zinc until the solution became colorless. Then the solution was filtered and the filtrate was diazotized with 3.6 g of sodium nitrite in 50 ml of water at low temperature. The end of the diazotization was monitored with a potassium iodide-starch paper. After 0.5 h at 0 °C, the solution was extracted with ether. The residue obtained after evaporation of the solvent was dissolved in 10 ml of acetic acid and refluxed for 5 h. After evaporation of the solvent, the product was chromatographed on silica gel to give pale brown needles, 1.7 g (21%), mp 183—184 °C (lit,[18] 181 °C).

2-(Hydroxymethyl)phenyl Phenyl Selenide. This compound was prepared through reduction of 2-(phenylseleno)benzoic acid with lithium aluminium hydride. The details will be described elsewhere.

The authors thank Professor Hiizu Iwamura of IMS for his helpful discussion.

References

1) For a review see H. Iwamura and W. Nakanishi, *Yuki Gosei Kagaku*, **39**, 795 (1981) and references cited therein.

2) W. McFarlane and R. J. Wood, *J. Chem. Soc., Dalton Trans.*, **1972**, 1397; J. E. Trend, Ph. D. Thesis, University of Wisconsin, Wisconsin, USA, 1976.

3) W. Nakanishi, S. Murata, Y. Ikeda, T. Sugawara, Y. Kawada, and H. Iwamura, *Tetrahedron Lett.*, **42**, 4241 (1981); W. Nakanishi, Y. Ikeda, and H. Iwamura, *J. Org. Chem.*, **47**, 2275 (1982); W. Nakanishi, S. Matsumoto, Y. Ikeda, T. Sugawara, Y. Kawada, and H. Iwamura, *Chem. Lett.*, **1981**, 1353; W. Nakanishi, Y. Ikeda, and H. Iwamura, *Org. Magn. Reson.*, **20**, 117 (1982).

4) H. J. Reich and J. E. Trend, *J. Chem. Soc., Chem. Commun.*, **1976**, 310.

5) Kalabin *et al.* also studied the orientational effect of lone pairs in ^2J(Se–C) of some seleno-substituted benzenes; see G. A. Kalabin and D. F. Kushnarev, *Zh. Struct. Khim.*, **20**, 617 (1979); G. A. Kalabin, D. F. Kushnarev, L. M. Kataeva, L. V. Kashurnikova, and R. I. Vinokurova, *Zh. Org. Khim.*, **14**, 2478 (1978).

6) W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Chem. Commun.*, **1973**, 10.

7) E. Breitmaier and W. Voelter, "^{13}C NMR Spectroscopy: Methods and Applications in Organic Chemistry," 2nd ed, Verlag Chemie, Weinheim (1978), pp. 92—110.

8) ^2J(Se–C(3,3′)) is identical with ^2J(Se–C(6,6′)).

9) W. Nakanishi, Y. Ikeda, and H. Iwamura, unpublished results. See also G. L. Nelson and E. A. Williams, *Prog. Phys. Org. Chem.*, **12**, 243 (1976).

10) A. Ruet and M. Renson, *Bull. Soc. Chim. Belges.*, **75**, 157 (1966); *Chem. Abstr.*, **65**, 3785 h (1966).

11) K. Sindelar, E. Svatek, J. Metysova, J. Metys, and M. Protiva, *Collect. Czech. Chem. Commun.*, **34**, 3792 (1969); *Chem. Abstr.*, **72**, 55224 t (1970).

12) R. Lesser and R. Weiss, *Ber.*, **47**, 2510 (1914).

13) R. Lesser and R. Weiss, *Ber.*, **46**, 2640(1913).

14) F. Krafft and A. Kaschau, *Ber.*, **29**, 443 (1896).

15) D. G. Foster, *Org. Synth.*, Coll. Vol. III, 771 (1955).

16) D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, **95**, 197 (1973).

17) M. T. Bogert and A. Stull, *J. Am. Chem. Soc.*, **49**, 2011 (1927).

18) S. Keimatsu and I. Satoda, *J. Pharm. Soc. Jpn.*, **55**, 1030 (1935).