The Structure of 2-Carboxyphenyl Methyl Selenoxide, Its Sodium Salt and Related Compounds in Solution, Studied by ^{1}H, ^{13}C and ^{77}Se NMR†

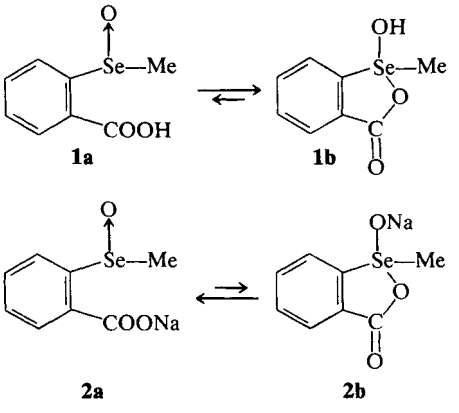
Warō Nakanishi* and Yoshitsugu Ikeda
Department of Chemistry, Faculty of Education, Wakayama University, Masago-cho, Wakayama 640, Japan
Hiizu Iwamura*
Division of Applied Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

^{1}H, ^{13}C and ^{77}Se NMR spectra of 2-carboxyphenyl methyl selenoxides, 2-carboxyphenyl phenyl selenoxides, their sodium salts and related compounds have been measured to determine their structures in solution. The ^{77}Se NMR chemical shifts and the $^{1}J(^{77}Se, ^{13}C)$ values were found to be particularly useful in distinguishing between selenuranes and selenoxides. The downfield shifts of 286–536 and 587–667 ppm from selenoanisoles are characteristic of the corresponding selenuranes and selenoxides, respectively. The couplings were 61–65 and 77–81 Hz for the selenuranes and selenoxides, respectively. The effects of salt formation on the NMR parameters are also discussed. The results show that the carboxylic acids have the cyclic selenurane structure, whereas the salts are acyclic selenoxides.

INTRODUCTION

Over the last 10 years, a number of new organoselenium compounds have been prepared and widely applied to organic synthesis.[2] The selenium atom is capable of attaining various coordination numbers and showing versatile reactivity, affording many structurally interesting compounds. The structural study of a series of organoselenium compounds by means of ^{77}Se NMR was first reported by McFarlane and Wood,[3] who found a regular dependence of chemical shifts on the electronegativity of the ligands. Trend[4] elaborated the above rule by examining the effects of discrete changes in the functionality at selenium in several selenides with more varied structures, and demonstrated the formation of tetracoordinated selenium species. Gronowitz *et al.*[5] and Kalabin *et al.*[6] studied the substituent effects in 4,4′-disubstituted diphenyl selenides and selenoanisoles, and Odom and co-workers[7] studied the relaxation time (T_1) of the selenium of some organoselenium compounds of biological interest. Thus, ^{77}Se NMR is becoming a powerful tool in elucidating the structure of organoselenium compounds.[8,9]

During the course of our investigation into the participation of the neighbouring selenium atom in the decomposition of *t*-butyl 2-methylselenoperoxybenzoate,[10] it became necessary to establish the structure of 2-carboxyphenyl methyl selenoxide (**1**).



1a **1b** **2a** **2b**

Since the carboxyl group in the neighbourhood of the Se—O bond can act as a fourth ligand to form a selenurane, **1** could be present as the selenoxide **1a** or the cyclic selenurane **1b**. Dahlén[11] has shown by x-ray crystallography that **1** has the ring closed selenurane structure with longer Se—O bonds; Trend[4] has reported, however, that **1** shows a ^{77}Se chemical shift characteristic of selenoxide **1a** in D_2O solution. It was felt that there had been no definitive NMR criterion which was able to differentiate unambiguously between a selenurane and a selenoxide. Therefore, we have examined the NMR spectra of a series of selenium compounds in order to find correlations with the structure. Based on these findings, we found that **1** should be represented as the cyclic selenurane **1b** *in* methanol or methanol-d_4 solution; the sodium salt (**2**) of **1** was also studied and found to have the acyclic structure **2a**.

* Authors to whom correspondence should be addressed.
† For a preliminary contribution, see Ref. 1.

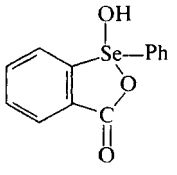
CCC-0030–4921/82/0020–0117$03.00

RESULTS AND DISCUSSION

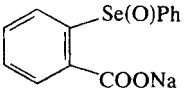
^{77}Se NMR chemical shifts

When the relevant ^{77}Se NMR chemical shifts [δ, referred to dimethyl selenide (**3**)] and data taken from the literature[12] are examined (Table 1), the chemical shifts for selenide anions, selenoles, selenides, selenonium salts, diselenides, selenuranes, selenoxides, selenones and other selenium-containing compounds are in the range shown in Fig. 1.[8] The chemical shifts for selenuranes and selenoxides are in the range δ 390–869 and δ 780–1000, respectively.[8] The range can be narrowed down if the structures are limited to selenoanisole derivatives of different oxidation states. In either case, the observed ^{77}Se chemical shift of **1** lies in the overlapping zone of the two groups of compounds.

The formation of selenuranes[13] from selenoanisoles (**4**) causes downfield shifts ($\Delta\delta$) in the range 286–536 ppm (with one exception of 639 ppm for a cyclic selenurane) depending on the electronegativity of the apical ligands (see Table 2). On the other hand, downfield shifts due to the formation of methyl phenyl selenoxides are in the range 587–667 ppm, depending on the nature of the 2-substituents. In this respect, the observed 527 ppm downfield shift of **1** from 2-methylselenobenzoic acid (**5**) is more consistent with cyclic structure **1b**. The structure of **2** with $\Delta\delta$ = 601 ppm is suggested to be **2a**. Similarly, the ^{77}Se chemical shifts of diphenyl selenoxide 2-carboxylic acid (δ 801) and its sodium salt (δ 849) are indicative of the selenurane (**15**) and selenoxide (**16**) structures, respectively.



15



16

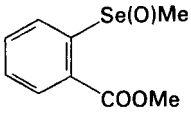
^{1}H and ^{13}C NMR chemical shifts and coupling constants

Structures **1b** and **2a** are further confirmed by comparing their ^{1}H and ^{13}C chemical shifts and ^{77}Se–^{13}C, ^{77}Se–^{1}H and ^{13}C–^{1}H coupling constants with those of related compounds (Table 3). NMR coupling constants between ^{77}Se and ^{13}C are known to be affected by the hybridization of the carbon atoms α to the selenium atom or the framework of organoselenium compounds. For example, ^{1}J(Se–*C) values of $PhCh_2{}^*CH_2SeCH_3$, $PhCH{=}{}^*CHSeCH_3$ and $PhC{=}{}^*CSeCH_3$ are 62.0, 115.5 and 187.4 Hz, respectively.[4] It is therefore necessary to choose appropriate compounds for comparison. Selenoanisole derivatives can, thus, be examined since only the change in coordination number of selenium of this series of compounds must be taken into account.

It was also thought necessary to study the ^{1}H and ^{13}C NMR parameters for the related 2-methylthio- and 2-methylsulphinylbenzoic acids and their sodium salts (Table 4) which have no tendency to form the cyclic sulphurane structure and, yet, are known to have a similar effect on the NMR parameters by salt formation. The carbonyl carbons of the sodium salts are shifted downfield by 5.8, 6.6 and 4.2 ppm from those of benzoic, 2-methylthiobenzoic and 2-methylsulphinylbenzoic acids, respectively.[14,15] The ring carbons bearing the carboxyl group (C-2 in Table 4) have large downfield shifts (7.4–10.4 ppm). The thio- and sulphinyl-substituted ring carbons (C-1 in Table 4) of the sodium salts are shifted upfield by 5.1 and 2.3 ppm from those of the free acids. Other parameters, such as the ^{1}H and ^{13}C chemical shifts and ^{1}J(CH) coupling constants, are independent of salt formation.

The methyl proton chemical shifts of 3- and 4-substituted selenoanisoles are characteristically in the region δ 2.1–2.4 (Table 3).[6] On the formation of selenuranes, as in **17** and **18**, *ca.* 1.5 ppm downfield shifts are induced due to the added electronegative ligands at selenium. The chemical shifts of the methyl group in selenoxides **12** and **13** are *ca.* δ 2.8, shifted approximately 0.5 ppm downfield from their parent selenides **4** and **6**, respectively. The ^{1}H chemical shift,

Table 1. ^{77}Se NMR chemical shifts[a]

Compound	No.	δ^{b}		Compound	No.	δ^{b}	
MeSeMe	(3)	0	0	$PhSeCl_2Ph$		586	
PhSeH		145	(152)[3]	$PhSe(OBz)_2Me$	(18)	672	(663)[4]
PhSeMe	(4)	202	(202)[4]	**1**		799[d]	(814)[4,e]
2-COOH	(5)	272	(265)[4]	**2**		826[d]	
2-COOMe	(6)	265		PhSe(O)Me	(12)	832	(830)[4]
2-COONa	(7)	225[c]			(13)	852	
PhSePh	(8)		(402)[35]				
2-COOH	(9)	470		PhSe(O)Ph	(14)	863	
2-COOMe	(10)	469		**15**		801[d]	
2-COONa	(11)	435[c]		**16**		849[d]	
PhSeSePh		475	(481)[7b]				

[a] Ppm in $CDCl_3$ unless otherwise stated.
[b] Literature values in parentheses.
[c] In 50% aqueous methanol.
[d] In methanol.
[e] In D_2O.

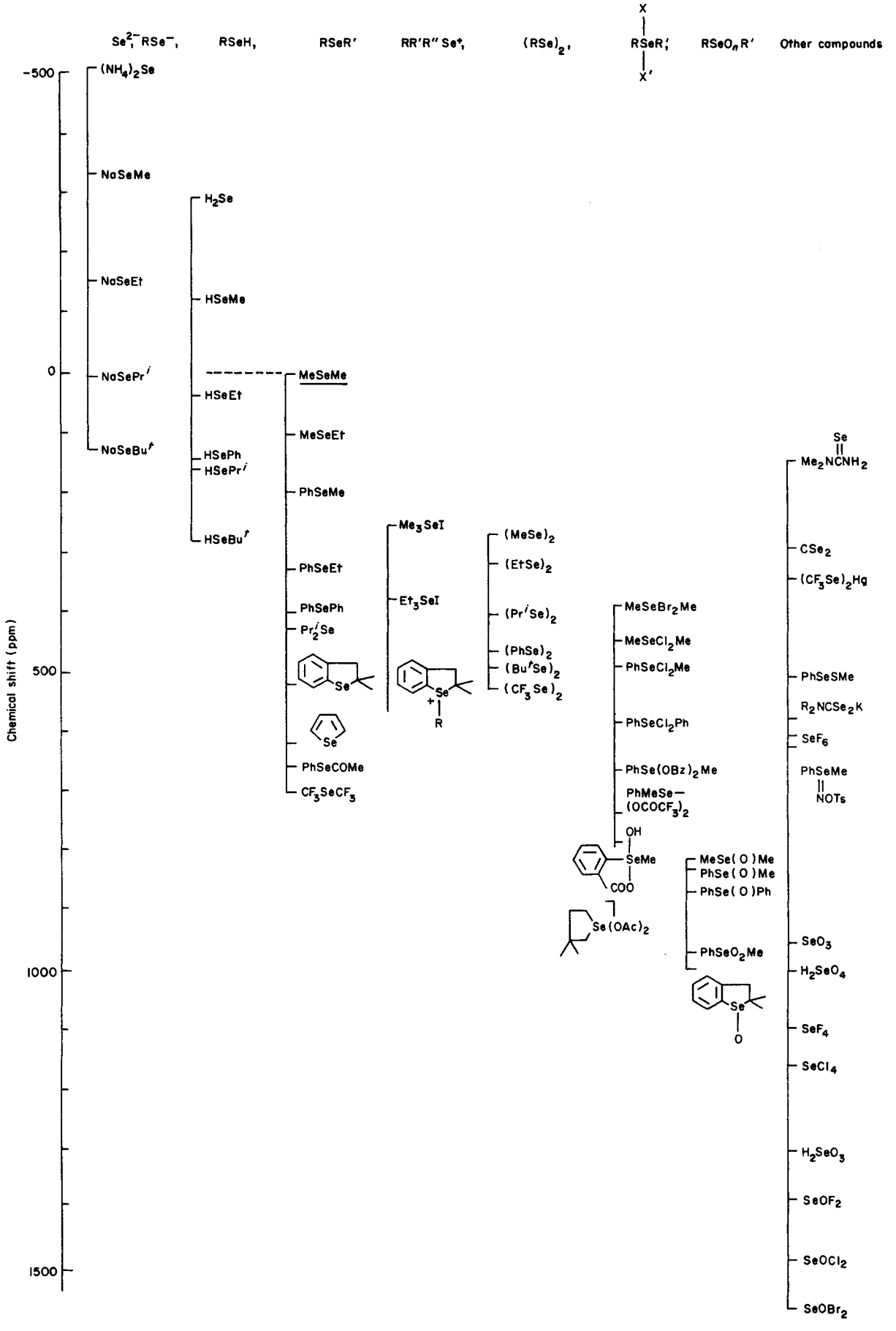
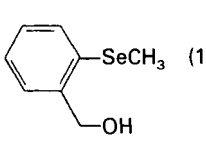
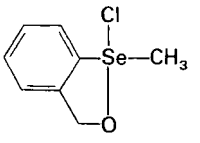
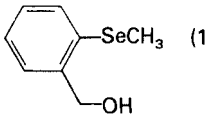
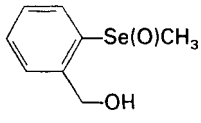
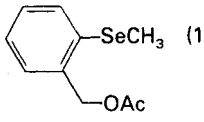
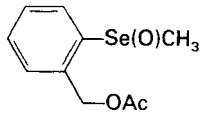


Figure 1. ^{77}Se NMR chemical shifts.

Table 2. ^{77}Se NMR chemical shift differences[a]

Compound	δ[b]	Compound	δ[b]	Δδ[c]
4	202	**17**	(488)[4]	286
		$PhSe(OAc)_2Me$	(658)[4]	456
		18	672,	470,
			(663)[4]	461
		$PhSe(OBu^t, Cl)Me$	(718)[4]	516
		$PhSe(OCOCF_3)_2Me$	(738)[4]	536
	(155)[4]		(794)[4]	639
	(155)[4]		(822)[4]	667
	(163)[4]		(816)[4]	653
4	202	**12**	832,	630,
			(830)[4]	628
6	265	**13**	852	587
5	272,	**1**	799,	527,
	(265)[4]		(814)[4]	549
7	225	**2**	826	601

[a] Chemical shifts in ppm are referred to MeSeMe (**3**).
[b] Literature values in parentheses.
[c] See text.

δ 3.17, of **1** is intermediate between selenuranes and selenoxides, while that of **2** (δ 2.80) is consistent with the acyclic structure **2a**.

The downfield shifts of the C-2 and carbonyl carbons of **7** from those of **5** are 9.3 and 6.1 ppm, respectively. The shift values of **2** from those of **1** are, however, 1.6 and 0.6 ppm, respectively. The magnitude of the shifts in the former corresponds very well to that of the sulphur analogues, whereas that of the latter does not. Thus, the structure of **2** seems again to be **2a**. The chemical shifts of **1** as a whole are not similar to those of 2-methylsulphinylbenzoic acid, suggesting that the structure of **1** is different from that of the sulphur analogue.

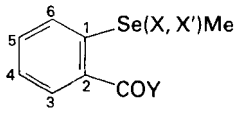
The most important parameter which appears to distinguish between selenuranes and selenoxides unambiguously is the one-bond coupling constant between ^{77}Se and ^{13}C, $^1J(Se, \underline{C}H_3)$. The values are in the range 61–65 Hz for selenuranes and 77–81 Hz for selenoxides (Table 3). The observed 65.1 Hz for **1** and 81.4 Hz for **2** are in the typical regions for a selenurane and selenoxide, respectively.

The $^2J(Se, \underline{C}H_3)$ values of selenuranes **17** and **18** and selenoxides **12** and **13** are 10.9, 10.1, 12.2 and 11.7 Hz, respectively. Those of **1** and **2** are 9.5 and 11.2 Hz, respectively. Since the $^2J(Se, \underline{C}H_3)$ values show a similar trend as for $^1J(Se, \underline{C}H_3)$, spin coupling between the selenium nuclei and protons is suggested to take place via the methyl carbons (i.e. a through-bond mechanism) in the methylseleno groups of selenoanisole derivatives.

The $^1J(CH)$ values of the methyl group also show

Table 3. ^{1}H and ^{13}C NMR data for organoselenium compounds

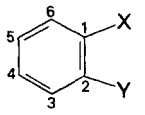
		Chemical shifts[b]									Coupling constants[c]			
Compound[a]	Solvent	H(Me)	C(Me)	C-1	C-2	C-3	C-4	C-5	C-6	C(CO)	^1J(SeMe)[d]	^2J(Se, C-6)[d]	^2J(SeMe)[e]	^1J(Me)[d]
3[f]	$CDCl_3$	2.00	6.0								60.4		10.1	140.6
4	$CDCl_3$	2.31	7.2	131.7	130.2	128.8	125.9	128.8	130.2		63.8	11.0	11.0	141.9
5	CD_3OD	2.21	6.0	139.3	129.3	132.4	124.8	133.3	127.9	169.6	68.2	6.6	14.4	140.5
6	CD_3OD	2.25	5.9	139.9	129.0	132.3	125.2	133.8	128.3	168.4	68.2	5.9	14.4	140.5
		(3.91[g])	(52.5[g])										(15.0[h])	(147.3[g])
7	CD_3OD	2.16	5.9	136.0	138.6	130.9	124.8	130.9	127.5	175.7	66.9	5.9	14.4	139.7
17	$CDCl_3$	3.90	45.7	141.0	128.5	129.9	131.7	129.9	128.5		61.0	13.2	10.9	149.0
18[i]	$CDCl_3$	3.73	35.8	138.9	129.6[j]	131.5[j]	132.3	131.5[j]	129.6[j]		64.5		10.1	146.8
12	$CDCl_3$	2.82	36.1	139.6	126.0	129.9	131.6	129.9	126.0		76.9	15.4	12.2	143.7
13	CD_3OD	2.78	38.1	145.5	129.1	132.0	132.4	135.6	126.0	168.6	80.6		11.7	144.4
		(4.01[g])	(53.8[g])											(148.4[g])
1	CD_3OD	3.17	40.2	138.5	134.8	133.5[j]	134.3	131.1[j]	127.2	171.7	65.1	6.0	9.5	147.3
2	CD_3OD	2.80	40.0	144.1	136.4	131.7	132.5	131.5	125.0	172.3	81.4	6.9	11.2	143.6

[a] The carbon numbering for **5**, **6**, **7**, **13**, **1** and **2** is as follows:  where (X, X') = (absent, absent) or (absent, O); Y = OH, OMe or ONa; (X, X'—Y) = (OH, O).

[b] Chemical shifts in ppm are referred to TMS.
[c] *J* values are in Hz.
[d] ≤ ± 0.7 Hz.
[e] ≤ ± 0.2 Hz.
[f] The $^3J(CH)$ value is 3.8 Hz.
[g] Data for methoxyl group.
[h] Proton coupled ^{77}Se NMR measurement.
[i] Chemical shifts of benzoyloxy groups are δ 132.3 (C-1'), 129.6 (C-2', 6'), 128.1 (C-3', 5'), 128.7 (C-4') and 170.6 (C'=O).
[j] Assignments are tentative.

Table 4. ^{1}H and ^{13}C NMR data for related organosulphur compounds

Compound[a]	Chemical shifts[b] H(Me)	C(Me)	C-1	C-2	C-3	C-4	C-5	C-6	C(CO)	Coupling[c] constants, ^1J(Me)
C_6H_5COOH			130.5	131.7	130.5	129.3	133.8	129.3	169.6	
C_6H_5COONa			130.0	139.1	130.0	128.4	130.9	128.4	175.4	
o-$MeSC_6H_4COOH$	2.44	15.4	144.5	128.3	132.4	124.3	133.5	125.4	169.5	138.8
o-$MeSC_6H_4COONa$	2.41	15.9	139.4[d]	138.7[d]	129.6[e]	124.6	130.0[e]	125.8	176.1	138.5
o-$MeS(O)C_6H_4COOH$	2.87	44.3	150.0	128.8	131.6[d]	134.8	132.3[d]	124.5	168.0	140.2
o-$MeS(O)C_6H_4COONa$	2.91	45.1	147.7	136.5	131.1[d]	131.4[d]	132.0[d]	123.5	172.2	140.0

[a] The carbon numbering is as follows; 

, X = absent, SMe or S(O)Me; Y = COOH or COONa.

[b] Ppm from TMS in CD_3OD.
[c] In Hz.
[d,e] Assignments are interchangeable.

clear-cut regions for selenuranes (147–149 Hz) and selenoxides (144 ± 0.4 Hz). Those of **1** and **2** are 147.3 and 143.6 Hz, respectively, supporting our conclusion. As the one-bond coupling constants of selenides are in the range 140–142 Hz, they make it possible to distinguish selenides from selenuranes and selenoxides.

The ^2J(SeC) values of selenoxide **12** and **2** are slightly larger than those of selenurane **17** and **1**, respectively. The two-bond coupling constants of **1** and **2** are, however, only about half the value of those of **17** and **12**. The coupling constants for **5**, **6** and **7** are also about half of that for **4**. As they appear to be governed not only by the oxidation state of the selenium atom but, also, by the orientation of the lone pair of electrons at selenium,[16–18] discussion on their correlation with structure is deferred until a further study is made on these series of compounds.

The possibility of a minor contribution from structure **1a** in **1** was checked from the ^{77}Se chemical shifts of **1** and **15**, which are nearly the same. As the substitution of the methyl with the phenyl group is usually accompanied by decreased shielding, the observed shift for **1** could be taken to be at too low a field to assign only structure **1b** to **1**. As shown in Table 5, however, no sign of any contribution from **1a** in equilibrium with **1b** was obtained from a change in environmental effects on the ^{1}H chemical shifts.

In conclusion, the structure of 2-carboxyphenyl methyl selenoxide **1** should be presented as the cyclic selenurane **1b**, not only in the solid state but also in methanol solution. The sodium salt (**2**) of **1** has the acyclic structure **2a**. To distinguish between the two structures, selenuranes and selenoxides, the ^{77}Se chemical shifts and the $^1J(^{77}Se, ^{13}C)$ values proved to be particularly useful. The ^1J(CH) values of the methyl group attached to the selenium atom are also informative.

Table 5. Temperature and solvent dependence of ^{1}H NMR chemical shift of methyl group of 1

Solvent	H(Me)[a]	Temp. (°C)	Solvent	H(Me)[a]	Temp. (°C)
CD_3OD	3.17	26	DMSO-d_6	3.07	26
	3.18	60		3.08	50
D_2O	3.09[b]	26		3.08	76
				3.08	101

[a] Ppm from TMS.
[b] Dioxane as δ 3.67.

The driving force for the selenurane formation in **1** is now found not necessarily to be crystal packing in the solid,[4,11] but its advantageous free energy of formation even in solution. Selenuranes are known to be formed where the electronegativity of the ligands at apical positions is larger than that of selenium,[13] and a greater number of electronegative ligands at the apical positions stabilize the selenuranes (for MO calculations for SH_4 see Ref. 19, and for sulphuranes see, for example, Ref. 20). The oxygen anion in **2b** may not be enough to stabilize the selenurane structure because the ligand is electron rich.[21]

EXPERIMENTAL

Spectral measurement

The ^{77}Se NMR spectra were obtained on a Varian FT-80A spectrometer, operating at 15.2 MHz, using a 90° pulse of 1 s. The spectral width was 8000 Hz, with 8K data points, and the number of transients accumulated was 10000. Field-frequency control (lock) was effected by means of the deuterium resonance of external D_2O. The shifts were determined relative to external dimethyl selenide (**3**).

The ^{1}H and ^{13}C NMR spectra were obtained on a JEOL FX-60Q spectrometer operating at 60 and 15 MHz, respectively. The spectral width was 1000 Hz with 8K data points for the ^{1}H NMR measurements. The ^{13}C NMR spectra were measured using a 60° pulse of 5 s; the spectral width was 3000 Hz, with 8K data points, and the number of transients was *ca.* 10000. Spectral widths of 600, 1000 and 3500 Hz and 30 or 45° pulses were also employed if necessary. The chemical shifts were determined relative to internal tetramethylsilane (TMS). The ^{77}Se–^{13}C and ^{77}Se–^{1}H coupling constants were measured by observing the ^{77}Se satellites in the ^{13}C and ^{1}H NMR spectra, respectively. The ^{13}C–^{1}H couplings were measured in the proton coupled mode. Selective decoupling was also applied for the assignments of ^{13}C chemical shifts if the conditions were satisfactory.

Approximately 100 mg of sample were dissolved in 1.5 ml of chloroform-*d*, methanol-d_4 or methanol. The sodium benzoate solutions were obtained by adding excess of sodium methoxide or aqueous sodium hydroxide to methanol-d_4 or methanol solutions of benzoic acid derivatives.

Compounds

Dimethyl selenide (**3**) was used as received (Tokyo Kasei Co., Ltd). The following compounds were prepared as described in the literature: 2-methylselenobenzoic acid (**5**),[22] diphenyl selenide (**8**),[23] 2-phenylselenobenzoic acid (**9**),[24,25] diphenyl selenide dichloride,[26] methyl phenyl selenoxide (**12**),[4] diphenyl selenoxide (**14**),[27] diphenyl selenone,[27] selenoanisole dichloride (**17**)[28] and selenoanisole dibenzoate (**18**).[29] The physical properties agreed well with those in the literature.

2-Methylseleninylbenzoic acid (1). One gram of **5**[22] was dissolved in 10 ml of methanol, treated with excess of hydrogen peroxide (35%) and the mixture refluxed for 4 h. A colourless solid was precipitated on addition of diethyl ether to the cooled reaction mixture. Recrystallization from ethanol gave 550 mg (51%) of colourless needles, m.p. 162–163 °C. Analysis: calculated for $C_8H_8O_3Se$, C 41.58, H 3.49; found, C 41.46, H 3.58%.

Methyl 2-methylseleninylbenzoate (13). *t*-Butyl hydroperoxide (22.5 mg, 2.5 mmol) was added dropwise to a solution of methyl 2-methylselenobenzoate (500 mg, 2.0 mmol; m.p. 63–64 °C; lit.[30] m.p. 64–66 °C; prepared by esterification of **5** with diazomethane in diethyl ether) in chloroform (16 ml), and the mixture was stirred for 20 h at room temperature. After removal of the solvent, the residue was crystallized from hexane to give 315 mg (55%) of the monohydrate of **13**, colourless needles, m.p. 115–116 °C ^{1}H NMR ($CDCl_3$) 2.60 (2H, s, H_2O), 2.65 (3H, s, CH_3), 3.98 (3H, s, CH_3), 7.5–8.7 (4H, m, C_6H_4). Analysis: calculated for $C_9H_{10}O_3Se{\cdot}H_2O$, C 41.08, H 4.60; found, C 41.28, H 4.36%.

2-Phenylseleninylbenzoic acid (15). Obtained as for **1**, or by oxidation of **9**[24,25] with concentrated nitric acid. Recrystallization from ethanol gave a more than a 70% yield of fine needles, m.p. 194.4–195.5 °C. Analysis: calculated for $C_{13}H_{10}O_3Se$, C 53.26, H 3.44; found, C 53.04, H 3.49%.

Acknowledgements

This work was supported by the Joint Studies Program (1980–81) of the Institute for Molecular Science. Thanks are due to Drs T. Sugawara and Y. Kawada for obtaining the ^{77}Se NMR spectra.

REFERENCES

1. W. Nakanishi, S. Matsumoto, Y. Ikeda, T. Sugawara, Y. Kawada and H. Iwamura, *Chem. Lett.* 1353 (1981).
2. N. Sonoda and K. Kondo, *Yuki Gosei Kagaku (J. Synth. Org. Chem. Jpn.)* **35**, 775 (1977); D. L. J. Clive, *Tetrahedron* **34**, 1049 (1978).
3. W. McFarlane and R. J. Wood, *J. Chem. Soc., Dalton Trans.* 1397 (1972).
4. J. E. Trend, Ph.D. Thesis, Wisconsin Univ. (1976).
5. S. Gronowitz, A. Konar and A.-B. Hörnfeldt, *Org. Magn. Reson.* **9**, 213 (1977).
6. G. A. Kalabin, D. F. Kushnarev, V. M. Bzesovsky and G. A. Tschmutova, *Org. Magn. Reson.* **12**, 598 (1979).
7. (a) W. H. Dawson and J. D. Odom, *J. Am. Chem. Soc.* **99**, 8352 (1977); (b) J. D. Odom, W. H. Dawson and P. D. Ellis, *J. Am. Chem. Soc.* **101**, 5815 (1979).
8. For a review, see H. Iwamura and W. Nakanishi, *Yiki Gosei Kagaku (J. Synth. Org. Chem. Jpn.)* **39**, 795 (1981), and references cited therein.
9. D. L. Klayman and W. H. H. Gunther (Eds), *Organic Selenium Compounds: Their Chemistry and Biology*, Wiley, New York (1973): (a) M. Lardon, p. 933; (b) U. Svanholm, p. 903.
10. W. Nakanishi, S. Murata, Y. Ikeda, T. Sugawara, Y. Kawada and H. Iwamura, *Tetrahedron Lett.* 4241 (1981); *J. Org. Chem.* **47**, 2275 (1982).
11. B. Dahlén, *Acta Crystallogr., Sect. B* **29**, 595 (1973).
12. See ref. 8, and references cited therein.
13. N. C. Baenziger, R. E. Buckles, R. J. Maner and T. D. Simpson, *J. Am. Chem. Soc.* **91**, 5749 (1969).
14. J. B. Stothers, *Carbon-13 NMR Spectroscopy*, p. 295. Academic Press, New York (1972).
15. E. Breitmaier and W. Voelter, *^{13}C NMR Spectroscopy: Method and Applications in Organic Chemistry*, 2nd Ed., p. 187. Verlag Chemie, Weinheim (1978).
16. W. McFarlane and D. S. Rycroft, *Chem. Commun.* 10 (1973).
17. H. J. Reich and J. E. Trend, *Chem. Commun.* 310 (1976).
18. G. A. Kalabin and D. F. Kushnarev, *Zh. Struct. Khim.* **20**, 617 (1979); G. A. Kalabin, D. F. Kushnarev, L. M. Kalaeva, L. V. Kashurnikova and R. I. Vinokurova, *Zh. Org. Khim.* **14**, 2478 (1978).
19. M. M. L. Chen and R. Hoffmann, *J. Am. Chem. Soc.* **98**, 1647 (1976).
20. L. J. Adzima, E. N. Duesler and J. C. Martin, *J. Org. Chem.* **42**, 4001 (1977).
21. P. Livant and J. C. Martin, *J. Am. Chem. Soc.* **98**, 7851 (1976).
22. A. Ruwet and M. Renson, *Bull. Soc. Chim. Belg.* **75**, 157 (1966); *Chem. Abstr.* **65**, 3785h (1966).
23. H. M. Leicester, *Org. Synth., Coll. 2*, 238 (1943).
24. D. G. Foster, *Org. Synth., Coll. 3*, 771 (1955).
25. K. Sindelar, E. Svatek, J. Metysova, J. Metys and M. Protiva, *Collect. Czech. Chem. Commun.* **34**, 3792 (1969); *Chem. Abstr.* **72**, 55224t (1970).
26. H. M. Leicester, *Org. Synth., Coll. 2*, 240 (1943).
27. H. Rheinboldt and E. Giesbrecht, *J. Am. Chem. Soc.* **68**, 2671 (1946).
28. D. G. Foster and S. F. Brown, *J. Am. Chem. Soc.* **50**, 1182 (1928).
29. Y. Okamota, R. Homsany and T. Yano, *Tetrahedron Lett.* 2529 (1972).
30. R. Lesser and R. Weiss, *Chem. Ber.* **46**, 2640 (1913).

Received 12 February 1982; accepted (revised) 24 May 1982