

# Structure of bis[8-(phenylselanyl)naphthyl] diselenide: first linear alignment of four Se atoms as a four-centre six-electron bond

Warō Nakanishi,<sup>\*a</sup> Satoko Hayashi<sup>a</sup> and Shinji Toyota<sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Education, Wakayama University, 930 Sakaedani, Wakayama 640, Japan

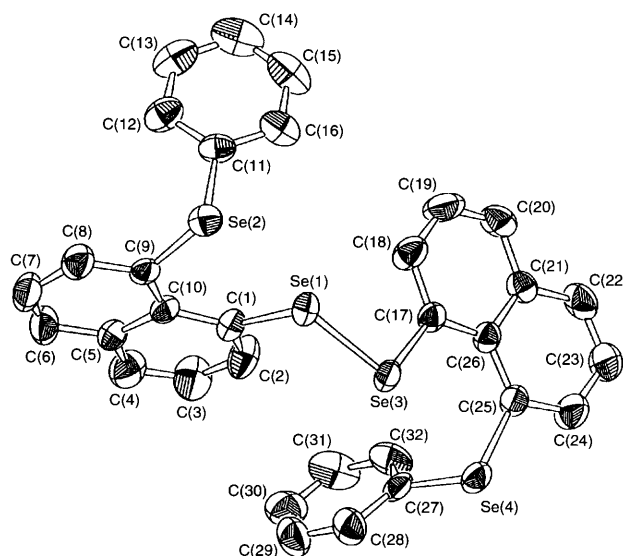
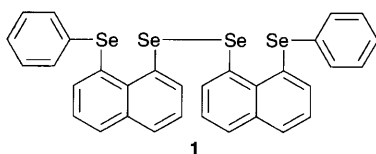
<sup>b</sup> Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Okayama 700, Japan

X-Ray crystallographic analysis of bis[8-(phenylselanyl)naphthyl] diselenide **1** reveals that the four selenium atoms in **1** align almost linearly with the angles of the adjacent three Se atoms 176.9 and 170.3°, respectively; the linear bond was shown to be a four-centre six-electron (4c–6e) bond by MO calculations.

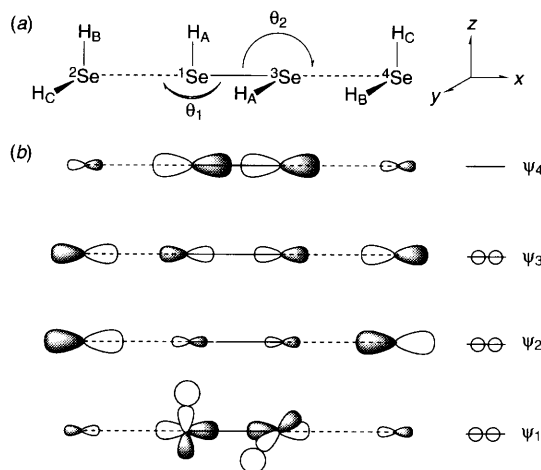
Nonbonded interactions between heteroatoms containing group 16 elements in the 1,8-positions of naphthalene are of current interest.<sup>1</sup> In the course of our investigation of such interactions, we obtained bis[8-(phenylselanyl)naphthyl] diselenide **1**† by treating the dianion of naphtho[1,8-*cd*]-1,2-diselenole with benzenediazonium chloride at low temperature.

X-Ray crystallographic analysis of **1**‡ revealed that the four selenium atoms in **1** align almost linearly. Fig. 1 shows the ORTEP diagram of **1**. The two naphthyl planes in **1** are almost perpendicular to each other. The torsional angle of *ca.* 90° for C(1)Se(1)Se(3)C(17) must resemble those in RSeSeR.<sup>2</sup> The naphthyl groups are orientated in a way that the four Se atoms align almost linearly, although they can rotate around the C(1)Se(1) and/or C(17)Se(3) bonds to avoid steric repulsion with the Se–Se bond. The angles of Se(3)Se(1)Se(2) and Se(1)Se(3)Se(4) and the torsional angle of Se(2)Se(1)–Se(3)Se(4) were found to be 176.9, 170.3 and 157.0°, respectively. Each phenyl group is located near the naphthyl group to which the phenyl group is not bonded (roof structure).

We wondered why the roof structure is more stable than the bent forms usually observed in polyselenides.<sup>3</sup> The effective interaction between the 4p-type lone pair orbitals of Se(2) and Se(4) atoms and the 4p–4p  $\sigma^*$ -orbital of the Se(1)–Se(3) bond is suggested by the average torsional angle of *ca.* 73° for C(10)C(9)Se(2)C(11) and C(26)C(25)Se(4)C(27). MO calculations with *ab initio* and semiempirical methods were performed on a model adduct to clarify the more stable linear structure.§ The simplified MO calculation model, H<sub>2</sub>Se–H<sup>1</sup>Se<sup>3</sup>SeH–<sup>4</sup>SeH<sub>2</sub>, is shown in Fig. 2(a). Two H<sub>A</sub>'s and H<sub>B</sub>'s are joined by 1,8-naphthylidene groups. H<sub>C</sub> represents a phenyl group. The atomic distances of *r*(<sup>1</sup>Se–<sup>3</sup>Se) were fixed as observed in **1** and those of *r*(<sup>1</sup>Se–<sup>2</sup>Se) and *r*(<sup>3</sup>Se–<sup>4</sup>Se) were fixed at the average value of the corresponding distances observed in **1** (2.365 and 3.053 Å respectively). The angles in HSeH and HSeSeH and the torsional angles in HSeSeH and those in the model were fixed at 90°. The MO's consisted of 4p<sub>x</sub>(Se)-orbitals based on PM3 with  $\theta_1$  and  $\theta_2$  fixed at 180° [Fig. 2(b)]. The  $\psi_3$  and  $\psi_4$  are predicted to be HOMO and LUMO, respectively.¶ These results show that the bond can be regarded as a four-centre six-electron (4c–6e) bond. This is also supported by the *ab initio* calculations.



**Fig. 1** Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Se(1)–Se(2) 3.019(1), Se(1)–Se(3) 2.365(1), Se(3)–Se(4) 3.087(1), Se(1)–C(1) 1.959(8), Se(2)–C(9) 1.911(8), Se(3)–C(17) 1.964(7), Se(4)–C(25) 1.903(8), C(1)–C(10) 1.42(1), C(9)–C(10) 1.42(1), C(17)–C(26) 1.42(1), C(25)–C(26) 1.42(1), Se(3)Se(1)C(1) 101.7(2), Se(1)Se(3)C(17) 103.2(2), Se(1)C(1)C(10) 122.3(6), C(1)C(10)C(9) 126.1(7), Se(2)C(9)C(10) 123.0(6), C(9)Se(2)C(11) 99.6(3), Se(3)C(17)C(26) 122.7(6), C(17)C(26)C(25) 127.5(7), Se(4)C(25)C(26) 124.8(6), C(25)Se(4)C(27) 100.7(3). Selected torsional angles (°): Se(1)C(1)C(10)C(9) 11(1), C(1)Se(1)Se(3)C(17) 91.0(3), Se(3)Se(1)C(1)C(10) 162.8(6), Se(2)C(9)C(10)C(1) 12(1), C(10)C(9)Se(2)C(11) 76.5(7), Se(3)C(17)C(26)C(25) 7(1), Se(1)Se(3)C(17)C(26) 178.5(6), Se(4)C(25)C(26)C(17) 6(1), C(26)C(25)Se(4)C(27) 69.7(7), C(9)Se(2)C(11)C(12) 51.3(8), C(25)Se(4)C(27)C(28) –162.4(7).



**Fig. 2** (a) Structure for MO calculations and (b) the 4c–6e bond model based on PM3 calculations with  $\theta_1$  and  $\theta_2$  being fixed at 180°

**Table 1** Predicted charges for H<sub>2</sub><sup>2</sup>Se-H<sup>1</sup>Se<sup>3</sup>SeH<sup>4</sup>SeH<sub>2</sub>, H<sub>2</sub>Se<sub>2</sub> and H<sub>2</sub>Se based on *ab initio* and semiempirical methods<sup>a</sup>

Method	$\theta_1(=\theta_2)^c$	H <sub>B</sub> H <sub>C</sub> <sup>2</sup> Se-H <sub>A</sub> <sup>1</sup> Se <sup>3</sup> SeH <sub>A</sub> <sup>4</sup> SeH <sub>B</sub> H <sub>C</sub> <sup>b</sup>							H <sub>2</sub> Se <sub>2</sub>	H <sub>2</sub> Se
		Q(H <sub>2</sub> Se <sub>2</sub> )	Q( <sup>1</sup> Se)	Q(H <sub>A</sub> )	Q(H <sub>2</sub> Se)	Q( <sup>2</sup> Se)	Q(H <sub>B</sub> )	Q(H <sub>C</sub> )	Q(Se)	Q(Se)
LANL1DZ	177.6	-0.096	-0.059	0.011	0.048	0.001	0.018	0.029	-0.032	-0.045
MP2/LANL1DZ	177.7	-0.096	-0.058	0.010	0.048	0.001	0.018	0.029	-0.031	-0.045
PM3	175.9	-0.224	-0.099	-0.013	0.112	0.117	-0.008	0.003	0.008	0.041

<sup>a</sup> Angles, together with torsional angles, were fixed at 90° (see text). <sup>b</sup> The optimized  $r(\text{Se-H})$  were 1.474 ± 0.002, 1.494 ± 0.004 and 1.476 ± 0.002 Å for LANL1DZ, MP2/LANL1DZ and PM3 respectively. <sup>c</sup> The predicted charges based on each method were equal to those given within ± 0.001, when  $\theta_1 = \theta_2 = 180^\circ$ .

The next extension of the calculations was to establish the character of the charge-transfer in the adduct and to optimize  $\theta_1$  and  $\theta_2$ , together with  $r(\text{Se-H})$ 's. The results are shown in Table 1. The nature of the charge-transfer in the 4c-6e bond is from the two outside H<sub>2</sub>Se's to the central H<sub>2</sub>Se<sub>2</sub>, which is essentially different from that of hypervalent 3c-4e bonds.<sup>4</sup> The MO calculations show that the driving force behind the linear alignment of the four Se atoms in **1** must be the energy lowering effect of the formation of the linear 4c-6e bond. The optimized values of  $\theta = ca. 180^\circ$  support this conclusion. Some linear bonds, such as X<sub>4</sub><sup>2-</sup> (X = I<sup>5a</sup> and Br<sup>5b</sup>), together with CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>--S<sup>+</sup>--S<sup>+</sup>--O<sub>3</sub>SCF<sub>3</sub><sup>6a</sup> and maybe I--Te--Te--I,<sup>6b</sup> must also be examples of this type of bond.

This work was supported by a Grant-in-Aid for Scientific Research (C) No. 05640608 from the Ministry of Education, Science, Sports and Culture, Japan.

#### Footnotes

† Elemental analyses were satisfactory for **1**. Yield 65.8%, mp 161–163 °C.  $\delta_{\text{H}}(\text{CDCl}_3)$ : 90 MHz) 7.0–7.5 (m, 14 H) and 7.6–8.2 (m, 8 H);  $\delta_{\text{C}}(\text{CDCl}_3)$ : 22.5 MHz) 125.9, 126.7, 127.6, 128.2, 128.3, 129.3, 130.3, 130.4, 131.0, 132.3, 135.6, 135.8, 136.3 and 139.0;  $\delta_{\text{Se}}(\text{CDCl}_3)$ : 69 MHz) 429.0 (*J* 341.4 Hz), 534.2 (*J* 341.4, 13.6 Hz).

‡ Crystal data for **1**: C<sub>32</sub>H<sub>22</sub>Se<sub>4</sub>, *M* = 722.37, primitive triclinic, *a* = 12.2175(8), *b* = 12.3430(8), *c* = 9.7474(8) Å,  $\alpha$  = 103.038(6)°,  $\beta$  = 110.715(5)°,  $\gamma$  = 91.791(6)°, *V* = 1329.5(2) Å<sup>3</sup>, space group *P* $\bar{1}$  (No. 2), *Z* = 2, *D*<sub>c</sub> = 1.80 g cm<sup>-3</sup>,  $\mu(\text{Cu-K}\alpha)$  = 67.5 cm<sup>-1</sup>. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu-K $\alpha$  radiation and a 12 kW rotating anode generator. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were included in fixed positions. The final cycle of full-matrix least-squares refinement was based on 3701 observed reflections (*I* > 2.50 $\sigma$ (*I*)) and 402 variable parameters and converged with unweighted and weighted agreement factors to give *R* = 0.056 and *R*<sub>w</sub> = 0.065 for independent observed reflections [Scan Type:  $\omega$ -2 $\theta$ , Scan Width: (1.73 + 0.30 tan  $\theta$ )°, 2 $\theta_{\text{max}}$  = 120.1°].

§ *Ab initio* MO calculations were performed by Gaussian 92 program<sup>7a</sup> with a LANL1 DZ basis set<sup>7b</sup> on a convex computer and semiempirical calculations were carried out at MOPAC PM3 level (ver. 6)<sup>8</sup> with GNORM = 0.01.

¶ Photoelectron spectroscopic studies on naphtho[1,8-*bc*]-1,5-dithiocin and 1,8-bis(methylsulfanyl)naphthalene showed that the HOMO of the former

was a  $\sigma^*$ -type orbital of the nonbonded S–S bond but that of the latter was the  $\pi^*$ -type orbital of the nonbonded S–S bond interacting with the  $\pi$ -orbital of the naphthalene ring.<sup>1a</sup>

#### References

- (a) R. S. Glass, S. W. Andruski and J. L. Broeker, *Rev. Heteroatom Chem.*, 1988, **1**, 31; R. S. Glass, S. W. Andruski, J. L. Broeker, H. Firouzabadi, L. K. Steffen and G. S. Wilson, *J. Am. Chem. Soc.*, 1989, **111**, 4036; R. S. Glass, L. Adamowicz and J. L. Broeker, *J. Am. Chem. Soc.*, 1991, **113**, 1065; (b) H. Fujihara, H. Ishitani, Y. Takaguchi and N. Furukawa, *Chem. Lett.*, 1995, 571; (c) H. Fujihara, M. Yabe, J.-J. Chiu and N. Furukawa, *Tetrahedron Lett.*, 1991, **32**, 4345; H. Fujihara, R. Saito, M. Yabe and N. Furukawa, *Chem. Lett.*, 1992, 1437; N. Furukawa, T. Fujii, T. Kimura and H. Fujihara, *Chem. Lett.*, 1994, 1007; (d) W. Nakanishi, *Chem. Lett.*, 1993, 2121.
- R. E. Marsh, *Acta Crystallogr.*, 1952, **5**, 458; F. H. Kruse, R. E. Marsh and J. D. McCullough, *Acta Crystallogr.*, 1957, **10**, 201; M. J. Potrzebowski, M. Michalska, J. Blaszczak, M. W. Wieczorek, W. Ciesielski, S. Kazmierski and J. Pluskowski, *J. Org. Chem.*, 1995, **60**, 3139.
- N. Takeda, N. Tokitoh, T. Imakubo, M. Goto and R. Okazaki, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2757; N. Tokitoh, *J. Synth. Org. Chem., Jpn.*, 1994, **52**, 136.
- G. C. Pimentel, *J. Chem. Phys.*, 1951, **19**, 446; J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 54.
- (a) E. Dubler and L. Linowsky, *Helv. Chim. Acta*, 1975, **58**, 2604; (b) R. Siepmann and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, 1968, **357**, 289.
- (a) H. Fujihara and N. Furukawa, *J. Mol. Struct. (Theochem)*, 1989, **186**, 261; (b) H. Fujihara, T. Uehara, T. Erata and N. Furukawa, *Chem. Lett.*, 1993, 263.
- (a) Gaussian 92, Revision C, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian Inc., Pittsburgh, 1992; (b) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
- (a) J. J. P. Stewart, Frank J. Seiler Res. Lab., US Air Force Academy, Colo. Spgs., CO 80840; (b) J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209; J. J. P. Stewart, *J. Comput. Chem.*, 1991, **12**, 320.

Received, 22nd September 1995; Com. 5/06262D