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SHORT COMMUNICATION

SYNTHESIS OF OPTICALLY ACTIVE 2,2′-DISELENOCYANATO-1,1′-BINAPHTHYL AND ITS MOLECULAR STRUCTURE. HYPERVALENT NATURE OF DIVALENT SELENIUM ATOM IN CRYSTAL STATE

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ABSTRACT

2,2′-Diselenocyanato-1,1′-binaphthyl(1), the first selenium-containing binaphthyl derivative, has been synthesized in optically active form from the corresponding diamine by diazotization followed by the reaction with potassium selenocyanate. Its molecular structure is determined by X-ray diffraction method. It is revealed that selenium atoms have hypervalent penta-coordination in the crystal.

Since the discovery of chiral recognition of a binaphthyl unit incorporated in crown ethers[1] the versatile of chiral binaphthyl compounds has been amply demonstrated in catalytic[2] or stoichiometric asymmetric synthesis[3] as well as in the development of technologically important materials such as nematic liquid crystals.[4] With the growing interest in this area, a number of efficient syntheses has been reported recently.[5] The binaphthyl compounds which have been prepared to date are, however, strictly limited to those possessing functional group(s) at 2 (and 2′)-position(s) which contain(s) second-row (C,N,O), third-row (S,Si) element(s) and/or halogens (Cl,Br). We wish to report herein the synthesis of the first monomeric selenium-containing binaphthyl, 2,2′-diselenocyanato-1,1′-binaphthyl(**1**) in optically active form and its molecular structure determined by X-ray diffraction method.

Initial attempts at the preparation of 1,1′-binaphthyl-2,2′-diselenide(**2**) by introduction of selenium metal into appropriate metallated (Li or MgBr) binaphthyl species failed to afford the desired compound presumably because **2** might undergo facile polymerization under the subsequent oxidative reaction conditions employed. We therefore selected the

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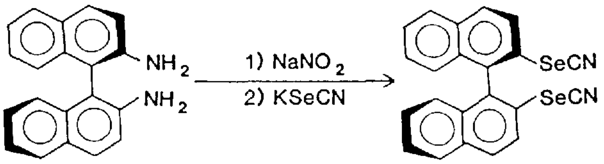


3 1

Scheme 1

diselenocyanate(**1**) as the target: the classical method of aryl selenocyanate synthesis was employed.[6] The synthesis procedure is as follows (Scheme 1).

Optically active diamine(**3**) was prepared by the literature method.[7] **R-3** was converted into optically pure **R-1** by diazotization followed by reaction with potassium selenocyanate according to the procedure reported previously.[6] After purification by silica gel chromatography (1:1 hexane-CH_2Cl_2), pure **R**-2,2′-diselenocyanato-1,1′-binaphthyl (**R-1**) was obtained in 24% overall yield. The optical purity of the pale yellow crystals (**R-1**) was unequivocally demonstrated by HPLC using an optically active (CHIRALPAK OT(+), Daicel, methanol as eluent). **R-1** (m.p.153–156°) showed characteristic spectroscopic behaviour(IR: 2155 cm^{-1} for CN; Se-NMR: 324·9 ppm for SeCN; C-NMR: 100·7 ppm for CN; UVmax: 225 nm ($e = 3{\cdot}4 \times 10^4$), $[\alpha]_D^{25}$: + 920° ($c = 0{\cdot}0012$ in CH_3CN)).

Single crystal X-ray analysis was performed for **R-1** which was repeatedly recrystallized from acetonitrile. A Rigaku automated 4-circle diffractometer was employed with the CuK_α radiation monochromatized by graphite. The crystal data obtained is as follows. $C_{22}H_{12}N_2Se_2$, M = 462·3, orthorhombic, $a = 16{\cdot}757(2)$, $b = 9{\cdot}683(1)$, $c = 11{\cdot}837(3)$Å, $U = 1920{\cdot}6$Å^3, space group $P2_12_12_1$, $Z = 4$, $D_c = 1{\cdot}58$ g/cm^3 (observed value; 1·59 g/cm^3). The structure was solved by the direct method and was refined by the full-matrix least-squares method neglecting hydrogen atoms. *R*-value was reduced to 0·090 for 1540 non-zero reflections. The ORTEP drawing is shown in Figure 1 and pertinent bonding parameters are collected in Table 1.

The two C(sp^2)-Se-C(sp)-N systems have similar bond lengths and bond angles within experimental error. The C(sp^2)-Se bond lengths are 1·97 and 1·95Å, which are slightly longer than the value, 1·92Å, found in 1,4-diselenocyanatobenzene (**4**).[8] The C(sp)-Se bond lengths are 1·83 and 1·79Å, which are nearly identical to the corresponding bond length of **4**. One of the C(sp^2)-Se-C(sp) bond angles (91·5°) observed for **1** is somewhat lower than the normal C(sp^3)-Se-C(sp^3) bond angle (96·3° for dimethyl selenide).[9] The C—C bond length between the two naphthyl groups (1·46Å) is a little shorter than the corresponding value for binaphthyl (1·49Å),[10] which seems surprising since this bond is not lengthened by steric interaction between the two bulky selenocyanato moieties. It should be noted that one of the selenocyanato groups lies nearly in the plane of the naphthyl moiety to which it is bonded (dihedral angle: C(11)—C(2)—Se(1)—C(12); 6°), while the other clearly does not (C(31)—C(22)—Se(21)—C(32); 42°).

The dihedral angle between the two naphthyl groups is only 83° to our surprise, which is smaller than other binaphthyl compounds whose structures were previously determined by X-ray analysis: for example, the corresponding dihedral angles are 111°, 89°, and 85° for the 2,2′-X-substituted binaphthyls (X = OMe,[11] OH,[12] NH_2,[12] respectively). It may be predicted that the larger the substituents (X) are, the larger would be the dihedral angle between the two naphthyl groups if one considers intramolecular interaction in an isolated single molecule. However, the dihedral angle between the two bulky groups should also depend on the bond length of C—X and on the balance of force field in the crystal packing.

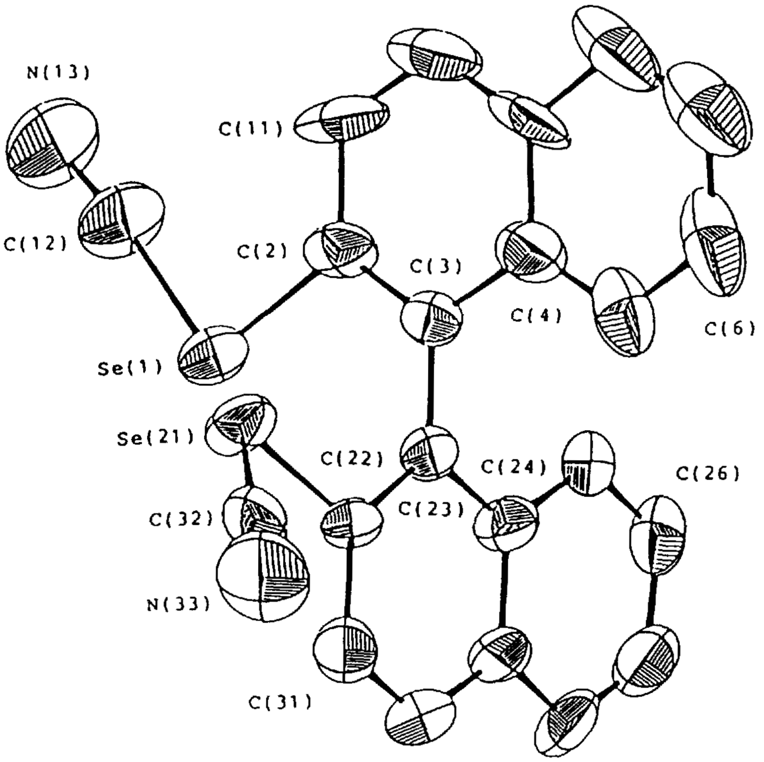


Figure 1. ORTEP drawing of **R-1**

Table 1. Pertinent bonding parameters for **R-1**

Bond Distances (Å)

C(2)—Se(1)	1·97(3)	C(22)—Se(21)	1·95(2)
Se(1)—C(12)	1·83(2)	Se(21)—C(32)	1·79(3)
C(12)—N(13)	1·15(4)	C(32)—N(33)	1·16(4)
C(3)—C(23)	1·46(3)		

Bond Angles (deg)

C(2)—Se(1)—C(12)	91·5(13)	C(22)—Se(21)—C(32)	96·6(11)
Se(1)—C(12)—N(13)	172(4)	Se(21)—C(32)—N(33)	177(3)

Dihedral Angles (deg)

C(2)—C(3)—C(23)—C(22)	80	C(2)—C(3)—C(23)—C(24)	97
C(4)—C(3)—C(23)—C(24)	86	C(4)—C(3)—C(23)—C(22)	98
C(11)—C(2)—Se(1)—C(12)	6	C(31)—C(22)—Se(21)—C(32)	42

A noteworthy feature in the crystal packing (orthorhombic) is the alignment of the selenium atoms which are located within 3·96Å along the *c* axis. These selenium atoms neatly align in a right-handed helix with the two kinds of regular distances between selenium atoms along the *c* axis (3·56Å for intramolecular selenium atoms and 3·96Å for intermolecular selenium atoms: the pitch of the helix corresponds to *c* (11·837Å), Figure 2). Since the van der Waals radius of Se is 2·0Å (Pauling's value), the aligned helical selenium atoms constitute a helical atomic wire in which the neighbouring selenium atoms are in contact with one another within its van der Waals radius.

It may also be pointed out that the selenium atoms possess some hypervalent nature. Thus Se(1) is situated near the aromatic carbon of the naphthyl moiety of the other diselenocyanate binaphthyl molecule (C(6′)) which is located along the *c*-axis: the distance between Se(1) and the nearest neighbouring carbon (C(6′)) in the other molecule is 3·44Å, which falls within the sum of van der Waals radii of carbon (1·7Å) and selenium (2·0Å). The C(6′)— Se(1)—C(2) bond angle is 161·4°, implying that these three atoms are approximately linearly aligned. Interestingly the Se(1), Se(21), C(12) and Se(21′) (the selenium-21 in the identical neighbor) not only lie approximately in the same plane, which is nearly perpendicular with respect to the C(6′)—Se(1) axis. Moreover, the bond angles involving these four atoms (Se(21)—Se(1)—Se(21′) = 130·0°, C(12)—Se(1)—Se(21′) = 110·9°, and Se(21)—Se(1)—C(12) = 118·6°) strongly suggest the trigonal bipyramid form of Se(1) (Figure 3).

A somewhat different penta-coordinated hypervalent nature appears in the other selenium atom (Se(21)). As shown in Figure 4, the five atoms around Se(21) (C(22), Se(1), C(26′), C(32) and Se(1′)) constitute a pseudo square pyramid in which all non-bonded atoms are located within the sum of van der Waals radii. The arrangement of the four atoms around Se(21) (C(22), C(32), C(26′) and Se(1)) can be regarded roughly as a square base of the square pyramid whose pseudo axial vertex (Se(1′)) is situated at 3·96Å away from the central selenium atom (Se(21)) with the bond angles C(26′)—Se(21)—Se(1′) = 91·3°, Se(1)—Se(21)—Se(1′) = 128·1° etc. Since the energy difference between trigonal bipyramidal and square pyramidal structures in penta-coordinate organometallic complexes is generally small,[13] it is understandable that the selenium atoms in **1** take either hypervalent structure in the crystalline state.

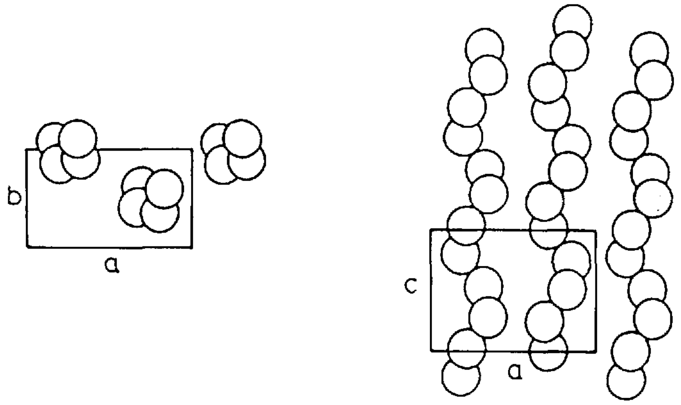
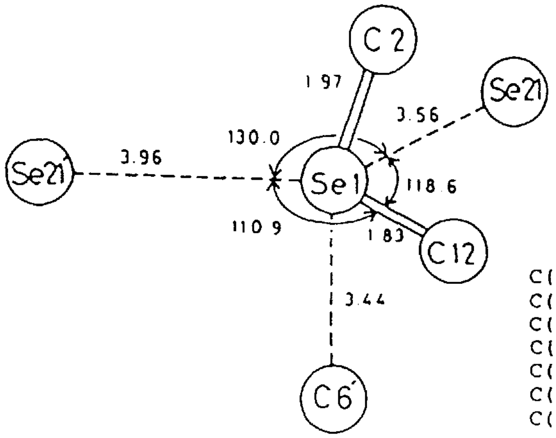
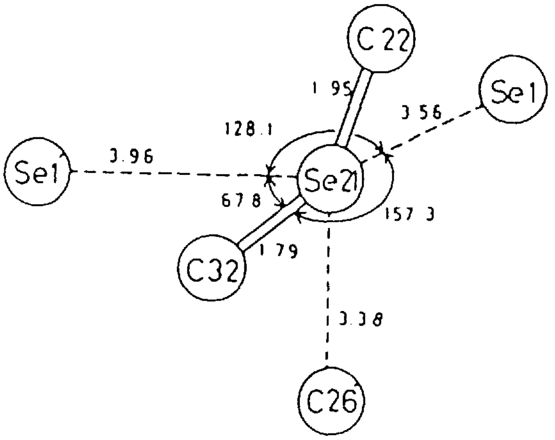


Figure 2. The helical structure of selenium atoms in the crystal packing



	deg.
C(6')-Se(1)-C(2)	161.4
C(6')-Se(1)-Se(21)	93.8
C(6')-Se(1)-Se(21')	93.2
C(6')-Se(1)-C(12)	89.5
C(2)-Se(1)-Se(21)	69.5
C(2)-Se(1)-Se(21')	103.8
C(2)-Se(1)-C(12)	91.5

Figure 3. Hypervalent nature of Se(1) in the crystal of **1**



	deg.
C(26')-Se(21)-C(22)	164.5
C(26')-Se(21)-Se(1)	99.0
C(26')-Se(21)-Se(1')	91.3
C(26')-Se(21)-C(32)	96.3
C(22)-Se(21)-Se(1)	66.2
C(22)-Se(21)-Se(1')	101.6
C(22)-Se(21)-C(26')	96.6

Figure 4. Hypervalent nature of Se(21) in the crystal of **1**

To the best of our knowledge, this is the first example of hypervalent structure of a crystal of divalent selenium compound as revealed by X-ray diffraction analysis.

We are now trying to apply optically active **1** to asymmetric synthesis and to the synthesis of new functional substances.

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