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Crystal structure of *p*-ethoxyphenyl 2-(2-pyridyl)phenyl selenide

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Abstract

Crystals of *p*-ethoxyphenyl 2-(2-pyridyl)phenyl selenide consist of discrete diorganoselenium molecules with the selenium atom bonded to two different organo groups; Se–C bond distances, 1.932(4) and 1.929(4) Å and the C–Se–C angle 98.2(2)°. The Se...N separation of 2.813(6) Å indicates that there is no significant interaction between these atoms. Crystals are monoclinic, space group $P2_1/c$ with unit cell dimensions a 9.268(1), b 19.083(2), c 10.360(1) Å, β 114.59(1)°, $Z = 4$. The structure was refined by a full-matrix least-squares procedure to final $R = 0.023$ for 1328 reflections with $I \geq 2.5\sigma(I)$.

Introduction

This paper reports the preparation and single-crystal X-ray diffraction study of *p*-ethoxyphenyl 2-(2-pyridyl)phenyl selenide. The investigation forms a part of a wider study of related organotellurium(II) systems in our laboratories [1]. Our special objective in the case of the title compound was to compare its interatomic parameters with those determined previously for the analogous *p*-ethoxyphenyl 2-(2-pyridyl)phenyl telluride [1].

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Results

A molecule of *p*-ethoxyphenyl 2-(2-pyridyl) selenide (I), is shown in Fig. 1 and selected interatomic parameters are listed in Table 1. The selenium atom is bonded to two carbon atoms (Se–C(1) 1.932(4) and Se–C(12) 1.929(4) Å) derived from different organic substituents. The Se–C bond distances found in I are similar to the Se–C(Ph) bond distances found in the structure of [Ph$_2$Se$_2$][acac] (acac denotes the dinegative MeC(=O)CC(=O)Me anion) (there being two molecules in the crystallographic asymmetric unit) lie in the range 1.910(6)–1.927(5) Å, but are shorter than the Se–C(methine) bonds of 1.961(5)–1.991(5) Å in this compound, and those of 1.965(3) and 1.981(3) Å in the centrosymmetric [Se(acac)]$_2$ [2]. The C(1)–Se–C(12) angle is 98.2(2)°, which is larger than that (94.8(2)°) in the analogous tellurium complex, *p*-ethoxyphenyl 2-(2-pyridyl)phenyl telluride (II) [1]. The geometry found for the selenium(II) atom is entirely consistent with the presence of two stereochemically active lone-pairs of electrons. Of particular interest in the structure is the nature of the interaction between the pyridyl nitrogen atom and the selenium atom.

The Se...N separation, see Fig. 1, is 2.813(6) Å. This distance is greater than the sum of the covalent radii for these atoms of 1.87 Å but significantly less than the sum of the Van der Waals radii for these atoms of 3.5 Å [3]. However, as can be seen from Fig. 1 there is a twist about the C(6)–C(7) bond such that the nitrogen atom is directed away from the selenium atom. The selenium atom lies −0.0431(4) Å above the least-squares plane defined by the atoms C(1)–C(6), whereas the N(1) atom lies 0.669(3) Å below this plane. The dihedral angle between the C(1)–C(6) ring and the C(7)–N(1) ring is calculated to be 34.1° and the torsion angle C(1)C(6)C(7)N(1) is −33.6°. The geometric evidence overwhelmingly indicates that there is no significant selenium to nitrogen bonding in I. A similar situation was reported for II, the Te...N separation of 2.695(4) Å in that was thought not to indicate significant bonding interaction between these atoms.

The remaining interatomic contacts show no abnormal features. The *p*-ethoxyphenyl ligand is planar within experimental error, and forms a dihedral angle of 83.7° with the least-squares plane through the C(1)–C(6) atoms.

Experimental

Preparation

p-Ethoxyphenyl 2-(2-pyridyl)phenyl selenide was prepared by a method similar to that for the tellurium(II) analogue [1].

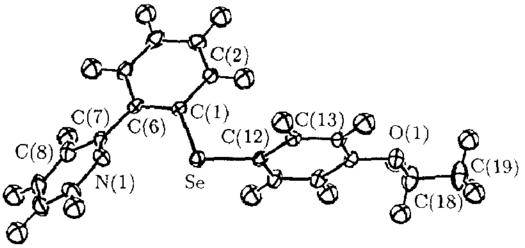

Fig. 1. Molecular structure and atom numbering scheme for *p*-ethoxyphenyl 2-(2-pyridyl) selenide. Hydrogen atoms are labelled according to the carbon atom to which they are bonded.

Table 1

Selected bond distances (Å) and angles (°) for *p*-ethoxyphenyl 2-(2-pyridyl) selenide.

Se–C(1)	1.932(4)	Se–C(12)	1.929(4)
C(1)–C(2)	1.391(5)	C(2)–C(3)	1.385(6)
C(3)–C(4)	1.373(6)	C(4)–C(5)	1.370(6)
C(5)–C(6)	1.385(5)	C(1)–C(6)	1.402(5)
C(6)–C(7)	1.474(5)	N(1)–C(7)	1.331(5)
C(7)–C(8)	1.396(5)	C(8)–C(9)	1.369(7)
C(9)–C(10)	1.358(7)	N(1)–C(11)	1.344(5)
C(10)–C(11)	1.367(6)	C(12)–C(13)	1.386(5)
C(13)–C(14)	1.368(5)	C(14)–C(15)	1.385(5)
C(15)–C(16)	1.383(5)	C(16)–C(17)	1.379(6)
C(12)–C(17)	1.376(5)	O(1)–C(15)	1.365(4)
O(1)–C(18)	1.429(4)	C(18)–C(19)	1.477(6)
C(1)–Se–C(12)	98.2(2)	Se–C(1)–C(2)	119.7(3)
Se–C(1)–C(6)	120.7(3)	C(1)–C(6)–C(7)	122.3(3)
N(1)–C(7)–C(6)	116.3(3)	C(6)–C(7)–C(8)	122.6(4)
C(7)–N(1)–C(11)	118.3(4)	Se–C(12)–C(13)	120.6(3)
Se–C(12)–C(17)	121.7(3)		

A solution of 2-(2-pyridyl)phenylmercury(II) chloride (4.0 g, 0.01 mol) in chloroform (25 cm^3) was added to a solution of *p*-ethoxyphenylselenium bromide (prepared in situ from bis(*p*-ethoxyphenyl)diselenide (2.0 g, 0.005 mol) and bromine

Table 2

Crystal data and refinement details for *p*-ethoxyphenyl 2-(2-pyridyl) selenide

Formula	$C_{19}H_{17}NOSe$
Mol. wt.	354.3
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	9.268(1)
b, Å	19.083(2)
c, Å	10.360(1)
β, deg.	114.59(1)
Vol. (Å^3)	1666.1
Z	4
D_c (g cm^{-3})	1.413
F(000)	720
μ, cm^{-1}	22.03
Transmission factors (max/min)	0.663; 0.444
θ limits (°)	1.0–22.5
No. of data collected	2409
No. of unique data	2179
No. of unique reflections used with $I \geq 2.5\sigma(I)$	1328
R	0.023
k	1.75
g	0.0005
R_w	0.025
Residual ρ_{max} (e Å^{-3})	0.25

(0.8 g, 0.005 mol) at 0 °C in carbon tetrachloride under nitrogen). The mixture was stirred at room temperature for 2 h, after which the white solid was filtered off, washed with methanol, and dried in vacuo. The white material was suspended in ethanol (30 cm^3) and the solution treated dropwise with an excess of hydrazine hydrate then stirred for 15 min. Water (50 cm^3) was added and the solid filtered off then recrystallized from ethanol/acetone (1/1 v/v) to give pale yellow crystals of I. Yield (overall) 50%; m.p. 102–104 °C. Analysis: Found: C, 64.95; H, 4.83; N, 4.05. $C_{19}H_{17}NOSe$ calcd.: C, 64.25; H, 4.79; N, 3.94%.

Crystallography

Intensity data for 2409 reflections were measured on an Enraf–Nonius CAD4F diffractometer by use of graphite monochromatized Mo-K_α radiation and the $\omega/2\theta$ scan technique with a well-formed crystal 0.35 × 0.20 × 0.35 mm. No decomposition of the crystal occurred during the data collection. The data were corrected for Lorentz and polarization effects and for absorption [4]. Of the reflections measured (θ_{max} 22.5°) 2179 were unique (R_{amal} 0.014), and of these 1328 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability. Relevant crystal data and refinement details are given in Table 2.

The structure was solved by the Patterson method and refined by a full-matrix least-squares procedure based on F [4]. The non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model at their calculated positions. Refinement with a weighting scheme of the form $w =$

Table 3

Fractional atomic coordinates ($\times 10^5$ for Se; $\times 10^4$ for remaining atoms) for *p*-ethoxyphenyl 2-(2-pyridyl) selenide

Atom	x	y	z
Se	−20006(4)	24814(2)	20718(4)
O(1)	4046(3)	3909(2)	2523(3)
N(1)	−4354(4)	1654(2)	2371(3)
C(1)	−1309(4)	1518(2)	2231(3)
C(2)	−67(5)	1337(2)	1873(4)
C(3)	457(5)	649(2)	2014(5)
C(4)	−238(5)	142(2)	2505(5)
C(5)	−1458(5)	321(2)	2862(5)
C(6)	−2023(4)	1001(2)	2732(4)
C(7)	−3346(4)	1157(2)	3125(4)
C(8)	−3534(6)	819(3)	4240(5)
C(9)	−4758(6)	1016(3)	4573(5)
C(10)	−5763(6)	1536(3)	3836(6)
C(11)	−5531(5)	1838(3)	2741(5)
C(12)	−50(5)	2921(2)	2258(4)
C(13)	132(5)	3158(2)	1069(4)
C(14)	1492(5)	3487(2)	1183(3)
C(15)	2731(4)	3579(2)	2506(4)
C(16)	2583(5)	3346(2)	3709(4)
C(17)	1187(5)	3028(2)	3562(4)
C(18)	5350(6)	4029(3)	3861(5)
C(19)	6578(6)	4424(3)	3606(6)

$k/[\sigma^2(F)+g(F)^2]$ converged with final $R=0.023$, $R_w=0.025$, $k=1.75$ and $g=0.0005$.

Fractional atomic coordinates are listed in Table 3, and the numbering scheme used is shown in Fig. 1 (diagram drawn with the ORTEP program [5]). Scattering factors for neutral Se (corrected for f' and f'') were from ref. [6] and those for the remaining atoms were those incorporated in the SHELX76 program system [4]. A complete list of bond lengths and angles, a table of thermal factors, and a list of observed and structural angles are available from E.R.T.T.

Acknowledgements

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