

Synthesis and Crystal Structure of Hexahydrobis[(1,3-*p*-dimethylamino-benzyl)-1,3-diazepine]-2-selenone, C₂₃H₃₂N₄Se

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In the title compound, C₂₃H₃₂N₄Se, was synthesized and its crystal structure was determined by single crystal X-ray diffraction. The compound crystallizes in orthorhombic system, space group *Pbca*, *a* = 10.9960(10) Å, *b* = 14.9460(9) Å, *c* = 27.565(5) Å and *Z* = 2. According to X-ray crystallographic studies, the diazepine ring is observed to be in a disordered state. The site-occupancy of the major component refined to 0.53(1). The C–Se bond length of 1.862(4) Å is a double bond character. The dihedral angle between the two phenyl rings is 37.7(2)°.

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The use of exobicyclic alkenes of the type **1** (*m* = 2 or 3) as sources of *N*-heterocyclic carbene complexes of transition metals is well-established.¹ However, larger rings, *i.e.* *m* ≥ 4, have so far not been tackled. In an effort to fill the gap, we prepared **1c** (R = *p*-CH₂C₆H₄NMe₂; the R group was chosen so as to contain a quaternizable –NMe₂ functionality which would increase the water solubility). Under mild conditions, **1c** reacted with Group VI elements to give cyclic chalcogeno ureas (Eq. (1)). This behavior is typical of reactive tetraaminoalkenes **1a** and **1b**.^{2,3} In sharp contrast, **1c** is inert to electrophilic transition metal complexes such as [RuCl₂(η⁶-arene)]₂. This remarkable difference aroused our curiosity. Therefore, the X-ray structure of the seleno urea **2c**, derived from the alkene **1c** was determined.

In a typical reaction, bis[1,3-bis(*p*-dimethylaminobenzyl)-hexahydro-1,3-diazepine-2-ylidene] (**1c**: 0.886 g, 1.00 mmol) was heated with elemental selenium (0.200 g, 2.53 mmol) in refluxing toluene (20 mL) for 2 h. The resulting solution was cooled to room temperature and then filtered to remove the excess selenium. The volume of the filtrate was reduced to *ca.* 10 mL and hexane (10 mL) was added. Upon cooling the solution to –20°C, we obtained cream crystals of the title compound (0.54 g, 61%, m.p. = 141 – 142°). All reactions were carried out under argon atmosphere with the use of Schlenk techniques. The solvents were dried and deoxygenated by standard procedures. The new compound exhibited satisfactory spectroscopic and analytical data. ¹H NMR (CDCl₃): δ 1.34 (br, 4H, NCH₂CH₂CH₂N), 2.92 (s, 12H, CH₂C₆H₄N(CH₃)₂), 3.28 (br, 4H, NCH₂CH₂CH₂ CH₂N), 5.07 (s, CH₂C₆H₄NMe₂), 6.67 (d, 4H, CH₂C₆H₄NMe₂, *J* = 8.6 Hz), 7.28 (d, 4H, CH₂C₆H₄NMe₂, *J* = 8.6 Hz); ¹³C{¹H}NMR (CDCl₃) δ 24.30 (NCH₂CH₂CH₂ CH₂N), 40.50 (NCH₂CH₂CH₂ CH₂N), 50.41 (C₆H₄N(CH₃)₂), 61.5 (CH₂C₆H₄NMe₂), 112.4, 125.0, 129.6, 150.0 CH₂C₆H₄NMe₂, 192.8 (C–Se). *Anal.* Calcd. for C₂₃H₃₂N₄Se: C, 62.29; H, 7.27; N, 12.63; found: C, 60.15; H, 7.30; N, 12.39. The crystal and molecular structures of C₂₃H₃₂N₄Se were

determined by single crystal X-ray diffraction. The crystal data, details of the data collection and the structure determination are given in Table 1. The chemical reaction of the title compound is shown in Fig. 1. The structure was solved by direct methods and refined by full-matrix least squares. The non-hydrogen atoms were refined anisotropically. The diazepine ring proved to be disordered over two orientations. The site-occupancy of the major disordered component refined to 0.53(1). The relatively high *R* values are related to the weak scattering that is most probably a consequence of the disorder in the diazepine ring. H atoms were added at calculated positions and refined using a riding model with *U*_{iso}(H) = *xU*_{eq}(parent atom), where *x*

Table 1 Crystal and experimental data

Formula: C ₂₃ H ₃₂ N ₄ Se
Formula weight = 443.49
Crystal System: orthorhombic
Space group: <i>Pbca</i> <i>Z</i> = 8
<i>T</i> = 293(2)K
<i>a</i> = 10.9960(10) Å
<i>b</i> = 14.9460(9) Å
<i>c</i> = 27.565(5) Å
<i>V</i> = 4530.2(9) Å ³
<i>D</i> _x = 1.301 g cm ^{–3}
<i>μ</i> (Mo K _α) = 1.673 mm ^{–1}
Crystal size: (0.09 × 0.40 × 0.40) mm ³
Radiation (Mo K _α) = 0.71069 Å
Reflection collected = 4617
Independent reflections [<i>I</i> > 2σ(<i>I</i>)] = 2626
No. of parameters: 291
<i>R</i> = 0.061; <i>wR</i> = 0.18
<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.1185 <i>P</i>) ² + 0.1331 <i>P</i>] where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)
(Δ/σ) _{max} = 0.005
(Δρ) _{max} = 0.49 e Å ^{–3}
(Δρ) _{min} = –0.55 e Å ^{–3}
Measurement: Enraf Nonius CAD-4 Diffractometer
Program system: CAD-4 EXPRESS Software
Structure determination: Direct method with SHELXS-97
Refinement: Full matrix least-squares with SHELXL-97 in WINGX ⁵

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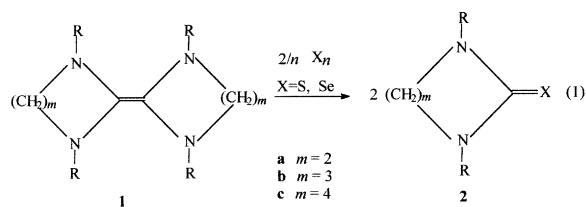


Fig. 1 The chemical reaction of the title compound.

Table 2 Final coordinates and equivalent isotropic displacement parameters of the non-H atoms for the title compound

Atom	x	y	z	U_{eq} (Å ²)
Se1	0.26058(4)	0.36493(4)	0.32121(2)	0.0919(3)
N1	0.3764(4)	0.2036(3)	0.2977(1)	0.111(2)
N2	0.5954(5)	0.1797(4)	0.5170(2)	0.127(2)
N3	0.3748(4)	0.3069(3)	0.2380(1)	0.097(2)
N4	0.0726(5)	0.5245(3)	0.0728(2)	0.120(2)
C1	0.3448(4)	0.2849(3)	0.2818(2)	0.085(2)
*C2A	0.414(2)	0.2597(10)	0.1958(5)	0.108(6)
#C2B	0.368(1)	0.2252(12)	0.1985(5)	0.070(4)
*C3A	0.4906(10)	0.1889(6)	0.1932(3)	0.086(3)
#C3B	0.379(2)	0.1651(10)	0.2029(5)	0.102(6)
#C4A	0.538(1)	0.168(1)	0.2439(7)	0.118(7)
*C4B	0.467(2)	0.1114(8)	0.2345(5)	0.103(5)
*C5A	0.5074(11)	0.1728(8)	0.2760(5)	0.081(4)
#C5B	0.444(2)	0.1295(10)	0.2756(6)	0.100(6)
C6	0.3221(6)	0.1624(4)	0.3404(2)	0.105(2)
C7	0.4015(4)	0.1659(3)	0.3852(2)	0.082(2)
C8	0.4880(5)	0.2298(3)	0.3929(2)	0.097(2)
C9	0.5538(5)	0.2348(3)	0.4356(2)	0.099(2)
C10	0.5327(5)	0.1765(3)	0.4732(2)	0.098(2)
C11	0.4446(5)	0.1109(3)	0.4657(2)	0.091(2)
C12	0.3827(5)	0.1055(3)	0.4219(2)	0.090(2)
C13	0.6864(7)	0.2486(5)	0.5235(3)	0.158(4)
C14	0.5458(10)	0.1422(5)	0.5601(3)	0.177(5)
C15	0.3948(4)	0.3985(4)	0.2211(2)	0.096(2)
C16	0.3088(4)	0.4323(3)	0.1829(2)	0.078(2)
C17	0.3518(4)	0.4797(3)	0.1430(2)	0.091(2)
C18	0.2753(4)	0.5119(3)	0.1074(2)	0.095(2)
C19	0.1495(4)	0.4959(3)	0.1097(2)	0.086(2)
C20	0.1069(4)	0.4484(3)	0.1496(2)	0.083(2)
C21	0.1847(4)	0.4181(3)	0.1852(2)	0.080(2)
C22	-0.0556(6)	0.5136(5)	0.0789(2)	0.131(3)
C23	0.1135(7)	0.5948(5)	0.0417(3)	0.155(3)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij}(a_i^* a_j^*)(a_i a_j)$$

*Site occupancy factor 0.53. #Site occupancy factor 0.47.

= 1.5 for methyl and 1.2 for others. The refined atomic parameters with equivalent isotropic temperature factors for non-hydrogen atoms are given in Table 2. Selected bond distances and bond angles are given in Table 3 and an ORTEP III drawing of the title compound together with the atomic numbering is shown in Fig. 2.

A notable feature of the ¹³C NMR spectrum of **2c** is a broad signal at δ 192.8 ppm assigned to C=Se group and shifted considerably to high frequency compared to previously known cyclic seleno ureas. This is in agreement with the substantial C=Se double bond [1.862(4)Å].⁴ The displacement parameters of atoms C2, C3, C4 and C5 of the diazepine ring are quite high, resulting in unusual bond lengths involving these atoms. As a result of the disorder, the average values of the N3-C2, C2-C3, C3-C4, C4-C5 and C5-N1 are 1.49(2), 1.13(2), 1.53(2), 1.07(2) and 1.56(1)Å, respectively. The distances between these partially populated sites of the C2A-C2B, C3A-C3B, C4A-C4B and C5A-C5B are 0.73(3), 1.30(2), 1.17(2) and 0.95(2)Å, respectively. The other bond lengths and angles are in agreement with those in the literature. The two partially populated sites of the diazepine ring are nonplanar.

The dihedral angle between the two phenyl rings is 37.7(2)° and each of the dimethylamino groups is tilted from the phenyl

Table 3 Selected bond lengths (Å) and bond angles (°) for C₂₃H₃₂N₄Se

Se1 - C1	1.862(4)	N3 - C2A	1.38(2)
N1 - C1	1.337(6)	N3 - C15	1.444(7)
N1 - C5A	1.63(1)	N3 - C2B	1.60(2)
N1 - C6	1.456(7)	N4 - C19	1.388(7)
N1 - C5B	1.46(2)	N4 - C23	1.429(9)
N2 - C10	1.391(8)	C6 - C7	1.515(7)
N3 - C1	1.351(6)	C15 - C16	1.503(7)
C1 - N1 - C5A	111.6(5)	C1 - N3 - C2B	114.0(7)
C6 - C7 - C8	123.5(4)	C15 - C16 - C17	120.8(4)
C1 - N1 - C5B	133.1(7)	C2A - N3 - C15	102.4(7)
C5A - N1 - C6	122.7(6)	C2B - N3 - C15	123.5(6)
N2 - C10 - C9	123.3(5)	C22 - N4 - C23	117.7(5)
C5B - N1 - C6	102.9(7)	Se1 - C1 - N3	120.8(3)
C13 - N2 - C14	116.2(6)	N1 - C1 - N3	117.7(4)
C1 - N3 - C2A	134.7(7)	N3 - C2A - C3A	129.6(12)
N3 - C15 - C16	114.8(4)	N1 - C5A - C4B	100.9(9)

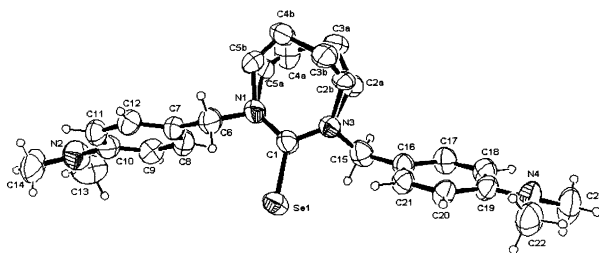


Fig. 2 An ORTEP drawing of the title compound showing the atomic numbering scheme. Displacement ellipsoids of non-H atoms are shown at the 30% probability level; H atoms are shown as small spheres of arbitrary size. H atoms of the diazepine ring have been omitted for clarity.

ring to which it is attached. The first dimethylamino group (C13-N2-C14) is tilted 22.3(6)° from the plane of its phenyl ring, while the second dimethylamino group (C22-N4-C23) is tilted 21.9(7)° from the plane of its phenyl ring. There are three intramolecular interactions: two of them are C-H...Se type and the other one is C-H...N type [C6...Se1 3.146(6), C6-H6B 0.970(7)Å and C6-H6B...Se1 109.6(3)°; C15...Se1 3.168(5), C15-H15B 0.970(5)Å and C15-H15B...Se1 113.9(3)°; C8...N1 2.924(6), C8-H8 0.930(5)Å and C8-H8...N1 100.6(3)°]. The molecules in the crystal are packed at normal van der Waals distances.

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