

Structure of 2-Benzoylamino-5-diethylamino-1,6,6a λ^4 -triseleno-3,4-diazapentalene

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The title compound C₁₄H₁₆N₄OSe₃ crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.364(1)$, $b = 11.723(1)$, $c = 17.122(2)$ Å, $\alpha = 90.803(8)$, $\beta = 101.783(9)$, $\gamma = 104.720(9)^\circ$ and $Z = 4$. The structure was refined to $R = 0.036$ for 4300 reflections with $F_o \geq 3\sigma(F_o)$. There are two symmetry-independent molecules per asymmetric unit which have nearly identical molecular structures. The 1,6,6a λ^4 -triseleno-3,4-diazapentalene part is nearly planar. The two Se–Se bonds in each molecule have different lengths. They are longer than Se–Se single bonds and their bond order is less than 1. The central C–Se bond is longer than the terminal C–Se bonds and has clearly single-bond character. The lengths of the C–N bonds in the rings and to the amino groups all lie between C–N single and double bonds and show π -electron delocalization in the molecule. The crystal structure is characterized by intermolecular Se...Se interactions and NH...N hydrogen bridges. The structure of the title compound shows a clear similarity to trithia- and triselenapentalenes and trithiadiazapentalenes.

The reaction of diethylamine with benzoylisoselenocyanate in acetone yields two different products according to the choice of treatment of the reaction mixture. Pouring the mixture on ice produces light-yellow 1,1-diethyl-3-benzoylselenourea, Et₂N–CSe–NH–CO–Ph, in high yield by nucleophilic addition.^{1–3} On the other hand, pouring the mixture into dilute cold hydrochloric acid, by analogy with the preparation of 1,1-dialkyl-3-benzoylthioureas,⁴ yields a precipitate with red and yellow components. After removal of the yellow 1,1-diethyl-3-benzoylselenourea with warm methanol, red crystals can be obtained by repeated extraction of the precipitate with chloroform at 35–40°C and concentration of the separated chloroformic phases by evaporation.⁵ The determination of the molecular structure of this red compound was the intention of our X-ray structure analysis. The results of this determination were, on the other hand, the starting point for the interpretation of ⁷⁷Se-NMR and ESCA investigations of this compound.⁵

Experimental

The crystals were prepared as described in detail elsewhere.⁵ Red needles of good quality suitable for X-ray investigation were obtained by recrystallization from acetonitrile. Unit cell dimensions and intensity data were measured on an automatic Enraf–Nonius CAD-4 diffractometer using a graphite monochromator and Mo K α radi-

ation ($\lambda = 0.71069$ Å). The unit cell dimensions were determined from 25 reflections ($9 < \theta < 21^\circ$) at room temperature. Intensities were checked by measurement of two reference reflections. Lorentz and polarization corrections were applied, but no absorption correction was made. Crystal and diffraction data are given in Table 1.

Table 1. Crystal and diffraction data.

Formula	C ₁₄ H ₁₆ N ₄ OSe ₃
M_r	493.2
M.p./°C	212–214
Space group	$P\bar{1}$
$a/\text{Å}$	9.364(1)
$b/\text{Å}$	11.723(1)
$c/\text{Å}$	17.122(2)
$\alpha/^\circ$	90.803(8)
$\beta/^\circ$	101.783(9)
$\gamma/^\circ$	104.720(9)
$V/\text{Å}^3$	1775.3
Z	4
$D_c/\text{g cm}^{-3}$	1.84
$F(000)$	952
μ/cm^{-1}	66.6
Crystal size/mm ³	0.15×0.20×0.25
Scan type	$\omega/2\theta$
2θ range/°	$2 < 2\theta < 52$
Measured reflections	6760
$ h_{\max} , k_{\max} , l_{\max} $	11, 13, 20
Observed reflections with $F_o \geq 3\sigma(F_o)$	4300
Final $R = \sum F_o - F_c /\sum F_o$	0.036

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Structure determination and refinement

The structure was solved by a combination of direct and Patterson methods. The two best E-maps were not directly interpretable because of pseudosymmetrical Se positions caused by errors in the sign determination process. Both E-maps, however, clearly showed a chain arrangement of Se atoms. Cross-checking with the Patterson synthesis and consideration of the lengths of the Se–Se bonds (about 2.6 Å) led to two different chains of three Se atoms. A subsequent electron-density map led in one of the two cases to the missing three Se atoms, but failed in the other case. The positions of the other non-hydrogen atoms were found from electron density maps derived subsequently. H atoms could be located with one exception (H143) from a difference Fourier map, but only H1 and H1' were included with these positions, whereas the other H atoms were included in calculated positions.

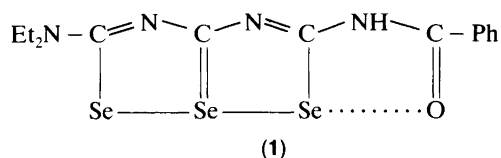
Blocked full-matrix anisotropic refinement of the non-hydrogen atoms with fixed H positions and *U*-values gave a final *R*-value of *R* = 0.036. The average and maximum Δ/σ were 0.004 and 0.016, respectively, and the final difference Fourier map peaks at 0.78 e Å⁻³ near a Se position.

Lists of calculated and observed structure factors, as well as H atom coordinates and other supplementary material, are available from one of the authors (R.R.) on request. All calculations were carried out with SHELX76;⁶ the drawings were made using ORTEP⁷ and PLUTO.⁸

Description of the structure and discussion

Rather unexpectedly, the investigated compound proved to be 2-benzoylamino-5-diethylamino-1,6,6aλ⁴-triselena-3,4-diazapentalene (1). There are two symmetry-independent molecules per asymmetric unit. The structure of these molecules is shown in Fig. 1. Atomic parameters are listed in Table 2 and bond lengths and angles in Table 3. Table 4 gives some selected torsion angles. In both molecules the triselenadiazapentalene parts are nearly planar (the maximum deviation for least-squares planes through all ring atoms is 0.21 Å for C1 in molecule 1 and 0.02 Å for C1' in molecule 2). Both molecules agree in all distances and angles, with the exception of the bond lengths between the Se atoms and the Se–Se–Se angle.

In both molecules the two Se–Se bonds are significantly different, with a longer Se–Se bond near the diethylamino group (2.641 and 2.582 Å) and a shorter Se–Se bond near the benzoylamino group (2.514 and 2.554 Å). One reason for this difference is to be seen in the different substituents on both sides of the triselenadiazapentalene



ring. In N-free triselenapentalenes with symmetrical substituents both Se–Se bond lengths are equal (in the range 2.542–2.586 Å).^{9–11} All Se–Se bonds are somewhat longer than the sum of the covalent radii (2.34 Å) but clearly shorter than the sum of the van der Waals radii (4.00 Å). The σ -bond order of the Se–Se bonds is, by analogy with the comparable trithiapentalene systems, less than 1.^{12–14} Therefore the Se–Se bond lengths are very sensitive to differences in the intramolecular substituents or to pertur-

Table 2. Atomic coordinates ($\times 10^4$) and equivalent temperature factors.

Atom	x	y	z	<i>U</i> _{eq} ^a
Molecule 1				
Se1	–4056(1)	5235(1)	1411(1)	0.063
Se2	–1329(1)	6007(1)	2334(1)	0.047
Se3	1137(1)	7098(1)	3230(1)	0.050
O1	3631(6)	9034(4)	3901(3)	0.050
N1	–2989(6)	7687(4)	1789(3)	0.033
N2	–598(6)	8519(4)	2440(3)	0.034
N3	1688(6)	9576(5)	3125(3)	0.037
N4	–5447(7)	7087(5)	1146(4)	0.049
C1	–4184(8)	6793(6)	1453(5)	0.043
C2	–1712(8)	7527(5)	2169(4)	0.034
C3	687(8)	8488(6)	2909(4)	0.037
C4	3155(8)	9800(6)	3558(4)	0.039
C5	4107(7)	11028(6)	3549(4)	0.036
C6	5381(8)	11415(7)	4163(5)	0.047
C7	6311(10)	12544(8)	4175(6)	0.061
C8	5981(11)	13265(8)	3571(6)	0.066
C9	4727(10)	12900(7)	2972(6)	0.060
C10	3778(9)	11770(7)	2952(5)	0.048
C11	–5521(9)	8331(7)	1210(5)	0.049
C12	–5778(14)	8704(9)	1998(7)	0.101
C13	–6828(12)	6206(9)	651(9)	0.100
C14	–7945(15)	5799(12)	1140(10)	0.135
H1	1246	10201	3011	0.040 ^b
Molecule 2				
Se1'	1508(1)	4262(1)	4775(1)	0.060
Se2'	71(1)	3780(1)	3304(1)	0.056
Se3'	–1308(1)	2950(1)	1886(1)	0.071
O1'	–2587(8)	1246(5)	555(3)	0.071
N1'	1284(6)	2007(5)	4104(3)	0.035
N2'	52(6)	1435(4)	2830(3)	0.036
N3'	–1140(7)	610(5)	1592(3)	0.040
N4'	2607(6)	2382(5)	5396(3)	0.041
C1'	1840(8)	2758(6)	4755(4)	0.038
C2'	521(8)	2273(5)	3443(4)	0.036
C3'	–760(8)	1572(6)	2134(4)	0.039
C4'	–1974(9)	502(6)	822(4)	0.043
C5'	–2057(9)	–592(6)	341(4)	0.042
C6'	–3338(10)	–1007(7)	–266(5)	0.052
C7'	–3473(12)	–2009(8)	–739(6)	0.068
C8'	–2351(14)	–2564(9)	–625(6)	0.082
C9'	–1069(12)	–2162(8)	–35(6)	0.072
C10'	–914(10)	–1157(7)	460(5)	0.051
C11'	2766(8)	1166(6)	5416(4)	0.045
C12'	1762(11)	414(8)	5916(6)	0.078
C13'	3389(10)	3167(7)	6130(5)	0.055
C14'	5004(10)	3796(9)	6084(6)	0.075
H1'	–859	–29	1808	0.040 ^b

^a*U*_{eq} = $\frac{1}{3}(U_{11} + U_{22} + U_{33})$. ^b*U*_{iso}.

Table 3. Distances (in Å) and angles (in °).

Molecule 1		Molecule 2	
Intramolecular distances			
Se1–Se2	2.641(1)	Se1'–Se2'	2.582(1)
Se1–C1	1.862(8)	Se1'–C1'	1.868(7)
Se2–Se3	2.514(1)	Se2'–Se3'	2.554(1)
Se2–C2	1.918(7)	Se2'–C2'	1.924(7)
Se3–O1	2.839(7)	Se3'–O1'	2.856(7)
Se3–C3	1.848(7)	Se3'–C3'	1.845(7)
O1–C4	1.209(9)	O1'–C4'	1.208(11)
N1–C1	1.344(8)	N1'–C1'	1.339(8)
N1–C2	1.300(9)	N1'–C2'	1.296(9)
N2–C2	1.352(7)	N2'–C2'	1.351(8)
N2–C3	1.313(8)	N2'–C3'	1.312(9)
N3–C3	1.371(7)	N3'–C3'	1.375(9)
N3–C4	1.378(8)	N3'–C4'	1.375(9)
N3–H1	0.93	N3'–H1'	0.91
N4–C1	1.324(10)	N4'–C1'	1.329(9)
N4–C11	1.481(10)	N4'–C11'	1.471(10)
N4–C13	1.519(11)	N4'–C13'	1.487(9)
C4–C5	1.490(9)	C4'–C5'	1.491(11)
C5–C6	1.390(9)	C5'–C6'	1.392(10)
C5–C10	1.390(11)	C5'–C10'	1.390(11)
C6–C7	1.385(11)	C6'–C7'	1.381(13)
C7–C8	1.381(14)	C7'–C8'	1.354(18)
C8–C9	1.361(12)	C8'–C9'	1.373(14)
C9–C10	1.390(10)	C9'–C10'	1.401(12)
C11–C12	1.496(15)	C11'–C12'	1.523(13)
C13–C14	1.461(21)	C13'–C14'	1.523(12)
Intramolecular angles			
Se2–Se1–C1	87.0(2)	Se2'–Se1'–C1'	87.7(2)
Se1–Se2–Se3	169.4(1)	Se1'–Se2'–Se3'	170.4(1)
Se1–Se2–C2	83.2(2)	Se1'–Se2'–C2'	84.3(2)
Se3–Se2–C2	86.4(2)	Se3'–Se2'–C2'	86.1(2)
Se2–Se3–O1	158.2(1)	Se2'–Se3'–O1'	158.3(1)
Se2–Se3–C3	87.7(2)	Se2'–Se3'–C3'	87.4(2)
O1–Se3–C3	71.0(2)	O1'–Se3'–C3'	71.0(3)
Se3–O1–C4	97.3(4)	Se3'–O1'–C4'	96.7(5)
C1–N1–C2	123.1(6)	C1'–N1'–C2'	123.2(6)
C2–N2–C3	122.0(6)	C2'–N2'–C3'	123.3(6)
C3–N3–C4	126.7(6)	C3'–N3'–C4'	127.2(6)
C3–N3–H1	113	C3'–N3'–H1'	113
C4–N3–H1	120	C4'–N3'–H1'	120
C1–N4–C11	120.7(6)	C1'–N4'–C11'	121.9(6)
C1–N4–C13	122.3(7)	C1'–N4'–C13'	122.4(6)
C11–N4–C13	116.8(7)	C11'–N4'–C13'	115.7(6)
Se1–C1–N1	121.7(6)	Se1'–C1'–N1'	121.4(5)
Se1–C1–N4	122.1(5)	Se1'–C1'–N4'	121.1(5)
N1–C1–N4	116.1(7)	N1'–C1'–N4'	117.5(6)
Se2–C2–N1	124.3(4)	Se2'–C2'–N1'	123.4(5)
Se2–C2–N2	119.8(5)	Se2'–C2'–N2'	119.9(5)
N1–C2–N2	115.8(6)	N1'–C2'–N2'	116.7(6)
Se3–C3–N2	123.1(4)	Se3'–C3'–N2'	123.2(5)
Se3–C3–N3	122.6(5)	Se3'–C3'–N3'	122.4(5)
N2–C3–N3	114.2(6)	N2'–C3'–N3'	114.4(6)
O1–C4–N3	121.5(6)	O1'–C4'–N3'	122.1(7)
O1–C4–C5	123.0(6)	O1'–C4'–C5'	122.6(6)
N3–C4–C5	115.5(6)	N3'–C4'–C5'	115.3(7)
C4–C5–C6	117.4(6)	C4'–C5'–C6'	116.7(8)
C4–C5–C10	122.6(6)	C4'–C5'–C10'	122.8(6)
C6–C5–C10	120.0(6)	C6'–C5'–C10'	120.5(7)
C5–C6–C7	119.5(7)	C5'–C6'–C7'	119.4(9)
C6–C7–C8	119.8(7)	C6'–C7'–C8'	120.2(9)
C7–C8–C9	121.2(8)	C7'–C8'–C9'	121.4(10)
C8–C9–C10	119.8(8)	C8'–C9'–C10'	119.6(10)
C5–C10–C9	119.7(7)	C5'–C10'–C9'	119.0(7)
N4–C11–C12	113.8(7)	N4'–C11'–C12'	111.9(7)
N4–C13–C14	109.8(11)	N4'–C13'–C14'	110.9(7)

contd.

Table 3. (contd.)

Intermolecular distances	
Se2 ... Se2' ^a	3.503(1)
Se2 ... Se3' ^a	3.660(1)
Se3 ... Se2' ^a	3.773(1)
Se1' ... Se1' ^b	3.859(1)
Se1 ... Se3' ^a	4.144(1)
Se3 ... Se1' ^a	4.317(1)
N3 ... N2' ^c	2.960(7)
H1 ... N2' ^c	2.03
N2 ... N3' ^c	2.967(7)
N2 ... H1' ^c	2.07

^a(*x*, *y*, *z*). ^b(–*x*, 1–*y*, 1–*z*). ^c(*x*, 1+*y*, *z*).

bations by the intermolecular environment. The latter influence should be responsible for the marked differences between the Se–Se bonds of the two symmetry-independent molecules. On the other hand, the triselenadiazapentale ring system is nearly planar, and therefore stabilized by delocalized π -bonds, by analogy with naphthalene. The bond situation is best described by the mesomeric structures 2–7 as already proposed for the 1,6,6a-trithia-3,4-diazapentalenes,¹⁵ with higher weights for structures 4 and 5.

The Se–O distance (2.839 and 2.856 Å) clearly exceeds the sum of covalent radii (1.83 Å), but is also shorter than the sum of van der Waals radii (3.40 Å). Therefore the O atom of the benzoylamino group is only slightly involved in the delocalized π -system of the triselenadiazapentale. The Se–Se–Se angle (169.4 and 170.4°) is smaller than in the triselenapentalenes (173.8, 175.2 and 178.9°).^{9–11} By analogy with the triselenapentalenes the central C–Se bond (1.918 and 1.924 Å) is longer than the two terminal C–Se bonds (1.862 and 1.868; 1.848 and 1.845 Å) and only minimally shortened in comparison with a C–Se single bond (1.94 Å), whereas the terminal bonds show partial double-bond character.

The C–N bond lengths in the ring system (1.296–1.352 Å) are alternating. All of them lie between C–N single (1.27 Å) and double (1.47 Å) bonds. The C–N bond between the ring system and the diethylamino group (1.324 and 1.329 Å) is also shortened in comparison with a single bond. The same is true for the C–N bonds to and in the

Table 4. Selected torsion angles (in °).

Molecule 1		Molecule 2	
C1–Se1–Se2–C2	–5.8(3)	C1'–Se1'–Se2'–C2'	1.2(3)
C2–Se2–Se3–C3	–6.4(3)	C2'–Se2'–Se3'–C3'	–0.1(3)
Se1–C1–N1–C2	–6.4(8)	Se1'–C1'–N1'–C2'	1.9(7)
Se2–C2–N1–C1	–1.4(8)	Se2'–C2'–N1'–C1'	–0.3(7)
Se2–C2–N2–C3	–9.4(7)	Se2'–C2'–N2'–C3'	–2.5(7)
Se3–C3–N2–C2	1.5(7)	Se3'–C3'–N2'–C2'	2.5(7)
Se3–C3–N3–C4	3.8(7)	Se3'–C3'–N3'–C4'	–1.5(8)
O1–C4–N3–C3	–11.8(8)	O1'–C4'–N3'–C3'	–6.4(9)

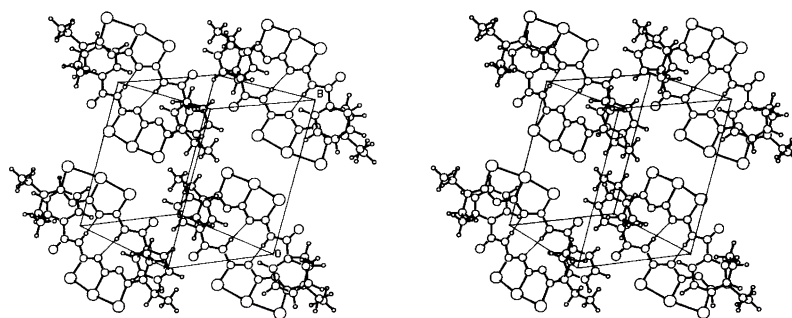


Fig. 2. Stereoscopic drawing showing the unit cell packing. The thin lines designate the $\text{NH}\cdots\text{N}$ hydrogen bonds in the structure.

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