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4,12-Diselena-5,6,13,14-tetraazatricyclo[9.3.0.0^{3,7}]-tetradeca-1(11),3(7),5,13-tetraene

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Keywords: crystal structure; heterocycle; selenium; medium-sized ring.

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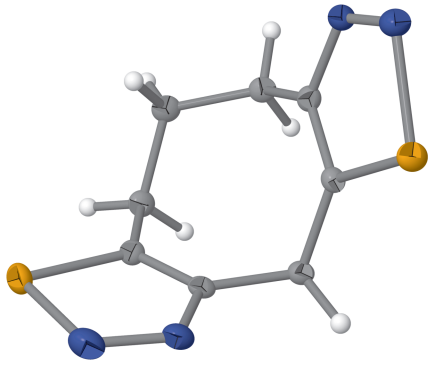
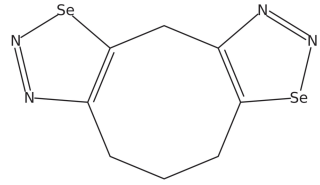
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_8H_8N_4Se_2$, two almost planar 1,2,3-selenadiazoles are annulated to a cycloocta-1,4-diene with a boat–chair conformation, giving the molecule a butterfly shape.

3D view



Chemical scheme



Structure description

The title compound, $C_8H_8N_4Se_2$, was prepared as part of a project focusing on medium-sized cycloalkynes with additional sterically demanding groups (Bissinger *et al.*, 1988; Detert *et al.*, 1994; Detert & Meier, 1997). Bis-1,2,3-selanadiazoles are important sources for medium-sized cycloalkadiynes (Gleiter *et al.*, 1988) and the structure of an isomer of the title compound has recently been reported (Detert & Schollmeyer, 2020). The tricyclic molecule adopts a butterfly-like shape with a boat–chair conformation of the eight-membered ring and two 1,2,3-selenadiazole rings are fused to the central ring (Fig. 1). Selenadiazole ring 1 (C2—N3—N4—Se5—C6) is planar within 0.003 (3) Å and selenadiazole ring 2 (C10—N11—N12—Se13—C14) within 0.008 (3) Å. While the connecting C1 atom lies above the plane of both selenadiazole rings [selenadiazole 1: 0.130 (3) Å; selenadiazole 2: 0.118 (3) Å], the adjacent C atoms of the propylene tether are either above these planes [C7: 0.037 (3) Å] or below [C9: −0.134 (3) Å]. The planes of the selenadiazole rings subtend a dihedral angle of 79.64 (13)°. Strain in the medium-sized ring is reflected in distortion of the bond angles on C7 [113.8 (3)°], C8 [115.8 (3)°] and C9 [118.4 (3)°], whereas a bond angle of 108.3 (2)° for C2—C1—C14 is close to the perfect tetrahedral angle. The packing diagram of the title compound is shown in Fig. 2.

Synthesis and crystallization

The title compound was prepared from cyclooctane-1,4-diol *via* Jones oxidation, formation of the semicarbazone and reaction with selenous acid in a 4.4% overall yield [m.p. 398–400 K (decomposition)]. Crystals were grown by slow evaporation of a solution

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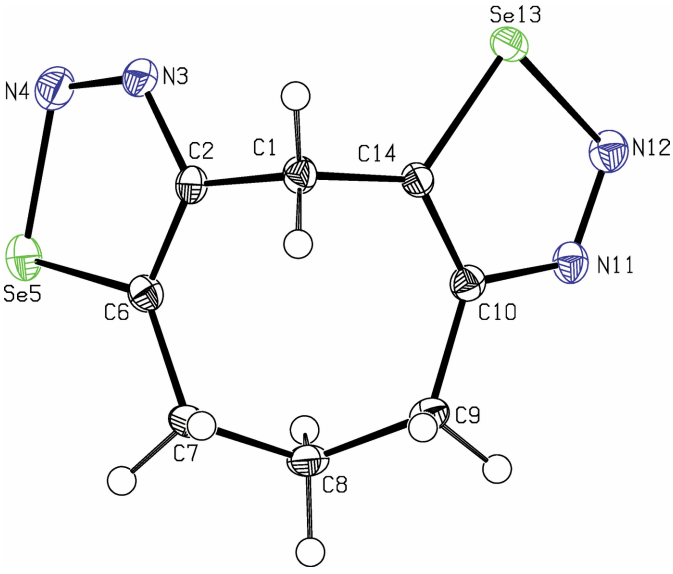

Figure 1
View of the title compound, with displacement ellipsoids drawn at the 50% probability level.

in chloroform–propan-2-ol. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.01 (*s*, 2H, H_2C-2), 3.25 and 3.10 (each: *t*, 2H, J = 6.6 Hz, H_2C-8,10), 1.95 (pseudo-*q*, 2H, H_2C-9). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 158.9, 156.4, 156.1 (C-1, 2, 7, 11); 26.7 (C-2), 26.4 (C-9), 25.7, 24.7 (C-8, 10) 41.5, 29.4, 28.5, 27.4, 25.5, 22.5, 20.0. ^{77}Se NMR (73 MHz, $CDCl_3$, SeO_2/D_2O as reference): δ 241.3, 240.7; UV (EtOH): λ (logε): 222 (4.09), 287 nm (3.45), MS (FD): 320 (M^+, Se_2-isotope pattern), 292 (M^+-N_2, Se_2-isotope pattern), 264 (M^+-N_2, Se_2-isotope pattern).

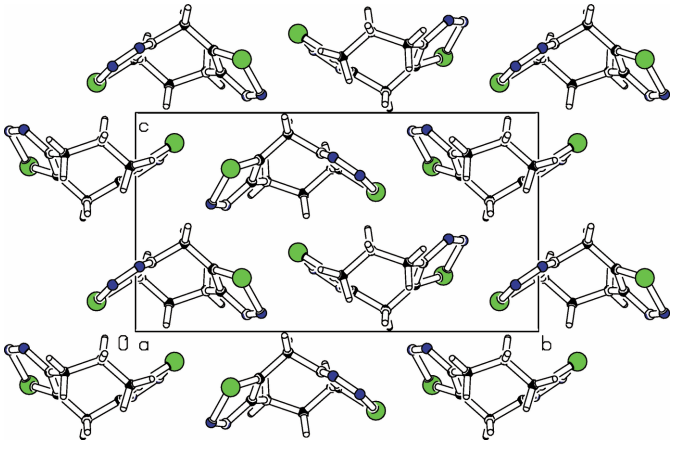

Figure 2
Part of the packing diagram, viewed along the *a*-axis direction.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_8H_8N_4Se_2$
M_r	318.10
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	120
a, b, c (Å)	7.2217 (4), 15.6664 (8), 8.4925 (5)
β (°)	90.110 (4)
V (Å^3)	960.82 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	7.66
Crystal size (mm)	0.42 × 0.31 × 0.21
Data collection	
Diffractometer	STOE IPDS 2T
Absorption correction	Integration
T_{min}, T_{max}	0.107, 0.251
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5404, 2296, 2066
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.660
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.071, 1.17
No. of reflections	2296
No. of parameters	127
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.44

Computer programs: *WinXpose* in *X-AREA* (Stoe & Cie, 2020), *Recipe* in *X-AREA* (Stoe & Cie, 2020), *Integrate* in *X-AREA* (Stoe & Cie, 2020), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2019* (Sheldrick, 2015*b*) and *PLATON* (Spek, 2020).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms attached to C atoms were placed at calculated positions and were refined in the riding-model approximation, with C—H = 0.99 Å and U_{iso}(H) = 1.2 U_{eq}(C).

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full crystallographic data

IUCrData (2025). **10**, x250324 [https://doi.org/10.1107/S2414314625003244]

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Crystal data

$C_8H_8N_4Se_2$
M_r = 318.10
Monoclinic, $P2_1/n$
a = 7.2217 (4) Å
b = 15.6664 (8) Å
c = 8.4925 (5) Å
β = 90.110 (4)°
V = 960.82 (9) Å^3
Z = 4
$F(000)$ = 608
D_x = 2.199 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 11184 reflections
θ = 2.7–28.3°
μ = 7.66 mm^{-1}
T = 120 K
Block, colorless
0.42 × 0.31 × 0.21 mm

Data collection

STOE IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12x0.4mm long-fine focus
Detector resolution: 6.67 pixels mm^{-1}
rotation method, ω scans
Absorption correction: integration
T_{min} = 0.107, T_{max} = 0.251
5404 measured reflections
2296 independent reflections
2066 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 28.0°, θ_{min} = 2.7°
h = −9→8
k = −20→20
l = −11→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.071
S = 1.17
2296 reflections
127 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0269P)^2 + 2.435P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4215 (4)	0.37887 (19)	0.9033 (4)	0.0160 (6)
H1A	0.302532	0.380853	0.960943	0.019*
H1B	0.522437	0.369867	0.980596	0.019*
C2	0.4515 (4)	0.46134 (19)	0.8159 (3)	0.0152 (6)
N3	0.6299 (4)	0.49038 (17)	0.7962 (3)	0.0178 (5)
N4	0.6528 (4)	0.55671 (18)	0.7130 (3)	0.0221 (6)
Se5	0.42162 (5)	0.59667 (2)	0.63795 (4)	0.02054 (10)
C6	0.3146 (4)	0.5069 (2)	0.7443 (4)	0.0157 (6)
C7	0.1118 (4)	0.4872 (2)	0.7445 (4)	0.0180 (6)
H7A	0.042450	0.539719	0.717557	0.022*
H7B	0.074926	0.469928	0.852125	0.022*
C8	0.0561 (4)	0.4161 (2)	0.6286 (4)	0.0185 (6)
H8A	−0.076361	0.423468	0.601538	0.022*
H8B	0.128039	0.423644	0.530446	0.022*
C9	0.0848 (4)	0.3240 (2)	0.6872 (4)	0.0171 (6)
H9A	0.039233	0.321004	0.796966	0.020*
H9B	0.004683	0.286199	0.623171	0.020*
C10	0.2770 (4)	0.2876 (2)	0.6847 (3)	0.0153 (6)
N11	0.3132 (4)	0.22323 (17)	0.5779 (3)	0.0175 (5)
N12	0.4723 (4)	0.18783 (17)	0.5841 (3)	0.0194 (5)
Se13	0.61533 (4)	0.23617 (2)	0.74477 (4)	0.01775 (9)
C14	0.4189 (4)	0.30689 (19)	0.7851 (3)	0.0141 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0178 (14)	0.0145 (14)	0.0158 (13)	0.0004 (11)	−0.0014 (11)	−0.0020 (11)
C2	0.0175 (14)	0.0135 (13)	0.0147 (13)	−0.0003 (11)	−0.0004 (11)	−0.0039 (11)
N3	0.0174 (13)	0.0166 (12)	0.0195 (12)	−0.0013 (10)	−0.0014 (10)	−0.0040 (10)
N4	0.0211 (14)	0.0207 (14)	0.0246 (14)	−0.0032 (11)	0.0018 (11)	−0.0046 (11)
Se5	0.02600 (18)	0.01483 (16)	0.02079 (16)	−0.00047 (12)	0.00078 (13)	0.00212 (11)
C6	0.0169 (14)	0.0152 (14)	0.0151 (13)	0.0011 (11)	0.0004 (11)	−0.0006 (11)
C7	0.0142 (14)	0.0180 (15)	0.0217 (15)	0.0037 (11)	−0.0019 (12)	−0.0011 (12)
C8	0.0120 (14)	0.0218 (16)	0.0217 (15)	0.0006 (11)	−0.0015 (12)	−0.0011 (12)
C9	0.0132 (14)	0.0198 (15)	0.0182 (14)	−0.0017 (11)	0.0005 (11)	−0.0005 (12)
C10	0.0157 (14)	0.0150 (13)	0.0152 (13)	−0.0011 (11)	−0.0002 (11)	0.0016 (11)
N11	0.0217 (13)	0.0156 (12)	0.0153 (12)	−0.0004 (10)	−0.0012 (10)	−0.0009 (10)
N12	0.0224 (14)	0.0193 (13)	0.0165 (12)	−0.0003 (11)	−0.0011 (10)	−0.0020 (10)
Se13	0.01585 (16)	0.01742 (16)	0.01997 (16)	0.00329 (11)	−0.00227 (11)	−0.00193 (11)
C14	0.0143 (14)	0.0125 (13)	0.0155 (13)	0.0007 (11)	0.0007 (11)	−0.0002 (10)

Geometric parameters (Å, º)

C1—C2	1.506 (4)	C7—H7B	0.9900
C1—C14	1.510 (4)	C8—C9	1.540 (4)

C1—H1A	0.9900	C8—H8A	0.9900
C1—H1B	0.9900	C8—H8B	0.9900
C2—C6	1.362 (4)	C9—C10	1.501 (4)
C2—N3	1.377 (4)	C9—H9A	0.9900
N3—N4	1.268 (4)	C9—H9B	0.9900
N4—Se5	1.892 (3)	C10—C14	1.366 (4)
Se5—C6	1.842 (3)	C10—N11	1.382 (4)
C6—C7	1.497 (4)	N11—N12	1.277 (4)
C7—C8	1.540 (4)	N12—Se13	1.870 (3)
C7—H7A	0.9900	Se13—C14	1.833 (3)

C2—C1—C14	108.3 (2)	C9—C8—C7	115.8 (3)
C2—C1—H1A	110.0	C9—C8—H8A	108.3
C14—C1—H1A	110.0	C7—C8—H8A	108.3
C2—C1—H1B	110.0	C9—C8—H8B	108.3
C14—C1—H1B	110.0	C7—C8—H8B	108.3
H1A—C1—H1B	108.4	H8A—C8—H8B	107.4
C6—C2—N3	116.8 (3)	C10—C9—C8	118.4 (3)
C6—C2—C1	124.4 (3)	C10—C9—H9A	107.7
N3—C2—C1	118.6 (3)	C8—C9—H9A	107.7
N4—N3—C2	117.5 (3)	C10—C9—H9B	107.7
N3—N4—Se5	110.0 (2)	C8—C9—H9B	107.7
C6—Se5—N4	87.31 (13)	H9A—C9—H9B	107.1
C2—C6—C7	126.9 (3)	C14—C10—N11	115.4 (3)
C2—C6—Se5	108.3 (2)	C14—C10—C9	126.9 (3)
C7—C6—Se5	124.7 (2)	N11—C10—C9	117.6 (3)
C6—C7—C8	113.8 (3)	N12—N11—C10	117.5 (3)
C6—C7—H7A	108.8	N11—N12—Se13	110.5 (2)
C8—C7—H7A	108.8	C14—Se13—N12	87.40 (13)
C6—C7—H7B	108.8	C10—C14—C1	126.1 (3)
C8—C7—H7B	108.8	C10—C14—Se13	109.3 (2)
H7A—C7—H7B	107.7	C1—C14—Se13	124.6 (2)

C14—C1—C2—C6	83.3 (4)	C7—C8—C9—C10	−78.1 (4)
C14—C1—C2—N3	−91.8 (3)	C8—C9—C10—C14	74.3 (4)
C6—C2—N3—N4	−0.2 (4)	C8—C9—C10—N11	−110.8 (3)
C1—C2—N3—N4	175.2 (3)	C14—C10—N11—N12	0.7 (4)
C2—N3—N4—Se5	−0.1 (3)	C9—C10—N11—N12	−174.7 (3)
N3—N4—Se5—C6	0.3 (2)	C10—N11—N12—Se13	0.2 (3)
N3—C2—C6—C7	178.3 (3)	N11—N12—Se13—C14	−0.8 (2)
C1—C2—C6—C7	3.1 (5)	N11—C10—C14—C1	174.7 (3)
N3—C2—C6—Se5	0.5 (3)	C9—C10—C14—C1	−10.4 (5)
C1—C2—C6—Se5	−174.7 (2)	N11—C10—C14—Se13	−1.3 (3)
N4—Se5—C6—C2	−0.4 (2)	C9—C10—C14—Se13	173.7 (2)
N4—Se5—C6—C7	−178.3 (3)	C2—C1—C14—C10	−75.3 (4)
C2—C6—C7—C8	−78.4 (4)	C2—C1—C14—Se13	100.0 (3)
Se5—C6—C7—C8	99.1 (3)	N12—Se13—C14—C10	1.1 (2)
C6—C7—C8—C9	82.1 (3)	N12—Se13—C14—C1	−174.9 (3)