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5,12-Diselena-3,4,13,14-tetraazatricyclo-[9.3.0.0^{2,6}]tetradeca-3,13-diene

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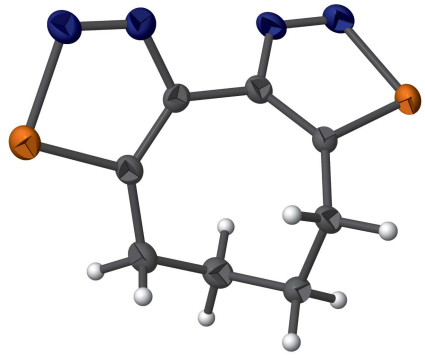
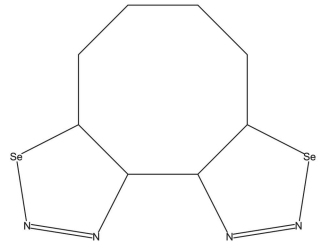
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_8H_8N_4Se_2$, crystallizes in a non-symmetrical conformation with a dihedral angle between the heterocycles of 45.0 (3)° and a nearly strain-free tetramethylene tether. The crystal studied was non-merohedrally twinned with a fractional contribution of 0.342 (3) for the minor twin component.

3D view



Chemical scheme



Structure description

1,2,3-Selenadiazoles are synthesized from SeO_2-oxdidation of semicarbazones (Yalpani *et al.*, 1971; Al-Smadi & Ratrout, 2004) and are important intermediates for the synthesis of medium-sized (Meier, 1972) heterocyclic (Detert, 2011) and strained cycloalkynes (Bissinger *et al.*, 1988). Bis-selenadiazoles have been used as intermediates for the synthesis of medium-sized cycloalkadiynes (Gleiter *et al.*, 1988).

The selenadiazole rings in the title compound (Fig. 1) are essentially planar and include a torsion angle of N13—C14—C4—N3 = −43.6 (10)°. This torsion angle is significantly smaller than the corresponding torsion angle (58.2°) in a dibenzocycloocta-1,3-diene (Janhsen *et al.*, 2017). In the tetramethylene tether, the dihedral angle at C8—C9—C10—C14 [84.9 (10)°] shows the largest deviation from the ideal value of 60° whereas C6—C7—C8—C9 matches this value nearly perfectly: −59.7 (11)°. Contrary to the formal symmetry, the conformer in the crystal shows neither a C_2 axis nor a mirror plane. Two molecules of the title compound fill the unit cell, and these are related by a center of inversion. One hydrogen atom at C7 points to the center of a selenadiazole of the neighbouring molecule, thus keeping the rings at a distance (Fig. 2).

Synthesis and crystallization

The title compound was prepared from cyclooctanone *via* oxidation with selenium dioxide to suberil, the formation of bis-semicarbazone and oxidation/cyclization with

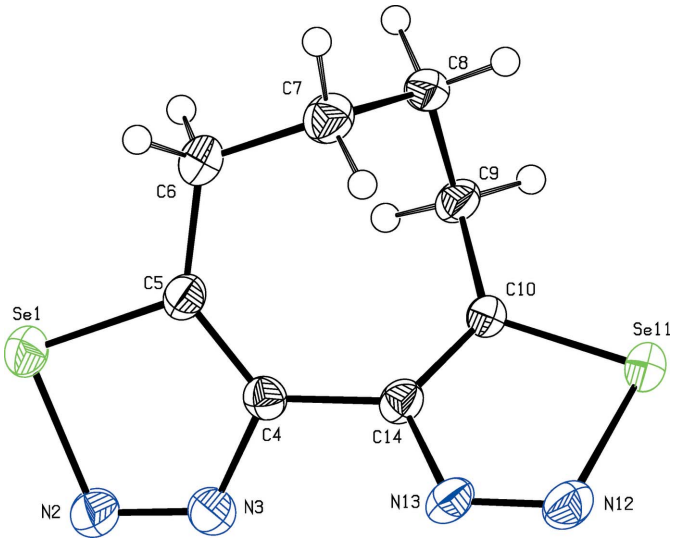


Figure 1
Perspective view of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

selenic acid. 5.1 g of bis-semicarbazone in 100 ml of 1,4-dioxane were stirred for 7 d after the addition of 6.6 g of SeO_2 in 10 ml of water. The mixture was concentrated to 60 ml, diluted with water (100 ml) and extracted with chloroform (2×). The pooled solutions were dried, concentrated and the residue purified *via* chromatography (SiO_2, toluene/ethyl acetate 10/1, R_f = 0.35). Recrystallization from the mixed solvents of chloroform/propanol-2 yielded colorless crystals with m.p. = 453 K (under explosion). ^{13}C NMR data are consistent with data given by Meier (Meier *et al.*, 1981)

^{1}H NMR ($CDCl_3$, 400 MHz) 3.15 (*broad s*, 4 H, H_2C-7, 10); 1.90 (*broad s*), 4 H, H_2C-8,9); ^{13}C NMR: 164.1, 151.9 (C-1,2,6,11), 26.8 (C-7, 10); 25.9 (C-8,9); IR (KBr): 2960, 1480, 1450, 1345, 1304, 1266, 844; ^{77}Se NMR ($CDCl_3$. 73 MHz, SeO_2/D_2O as reference): 238.9; ^{15}N NMR ($CDCl_3$, CH_3NO_2 as reference, 40.3 MHz): 87.1, 83.3; UV–vis (EtOH): 212 nm (4.,38), 243 (4.04), 297 (3.53); MS: *m*/*z* = 264 (17%, Se_2 pattern), 236 (17%, Se_2 pattern); 118 (21%, Se pattern), 104 (81%, C_8H_8); 103 (100%).

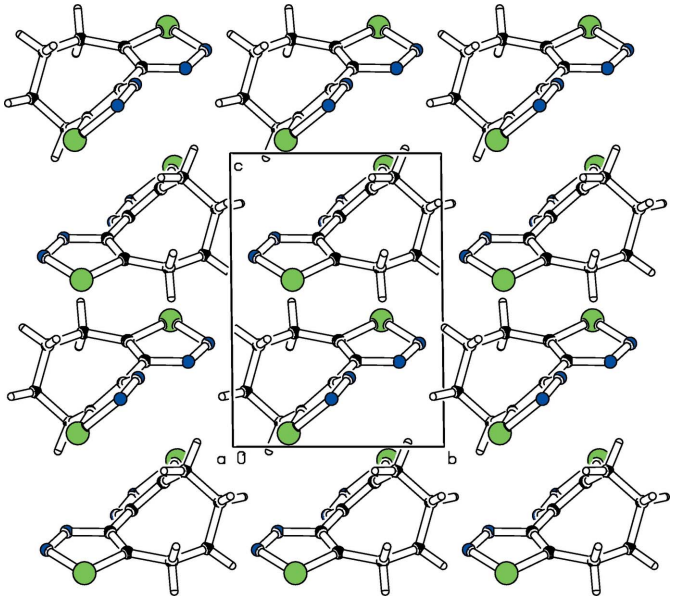


Figure 2
Partial packing diagram of the title compound. View is along the *b* axis.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_8H_8N_4Se_2$
M_r	318.10
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	120
a, *b*, *c* (Å)	7.5350 (18), 7.6723 (17), 9.372 (2)
α, β, γ (°)	90.136 (18), 90.773 (19), 118.555 (17)
V (Å^3)	475.8 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	7.73
Crystal size (mm)	0.45 × 0.23 × 0.22
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Integration
T_{min}, T_{max}	0.093, 0.252
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6775, 6775, 5946
R_{int}	0.046
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.666
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.217, 1.12
No. of reflections	6775
No. of parameters	128
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.68, −1.50

Computer programs: *X-AREA WinXpose*, *Recipe* and *X-AREA Integrate* (Stoe & Cie, 2019), *SIR2004* (Burla *et al.*, 2005), *SHELXL2018/3* (Sheldrick, 2015) and *PLATON* (Spek, 2020).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The crystal studied was non-merohedrally twinned with a fractional contribution of 0.342 (3) for the minor twin component.

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full crystallographic data

IUCrData (2020). **5**, x201585 [https://doi.org/10.1107/S2414314620015850]

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Crystal data

$C_8H_8N_4Se_2$
M_r = 318.10
Triclinic, $P\overline{1}$
a = 7.5350 (18) Å
b = 7.6723 (17) Å
c = 9.372 (2) Å
α = 90.136 (18)°
β = 90.773 (19)°
γ = 118.555 (17)°
V = 475.8 (2) Å^3
Z = 2
$F(000)$ = 304
D_x = 2.220 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5222 reflections
θ = 3.0–28.6°
μ = 7.73 mm^{-1}
T = 120 K
Needle, brown
0.45 × 0.23 × 0.22 mm

Data collection

Stoe IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration
T_{min} = 0.093, T_{max} = 0.252
6775 measured reflections
6775 independent reflections
5946 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 28.3°, θ_{min} = 3.0°
h = −9→9
k = −10→10
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.217
S = 1.12
6775 reflections
128 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1209P)^2 + 3.1505P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.68 e Å^{-3}
$\Delta\rho_{min}$ = −1.50 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.

Refinement. Refined as a 2-component twin.
Hydrogen atoms attached to carbons were placed at calculated positions and were refined in the riding-model approximation with C–H = 0.95 Å, and with U_{iso}(H) = 1.2 U_{eq}(C).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Se1	0.71557 (14)	0.29021 (14)	0.56893 (9)	0.0299 (3)
N2	0.4663 (14)	0.1129 (13)	0.6483 (9)	0.0330 (17)
N3	0.3899 (14)	0.2082 (12)	0.7102 (8)	0.0300 (16)
C4	0.4967 (13)	0.4132 (13)	0.7084 (8)	0.0219 (15)
C5	0.6788 (13)	0.4941 (14)	0.6393 (8)	0.0245 (16)
C6	0.8389 (16)	0.7040 (16)	0.6103 (10)	0.0323 (19)
H6A	0.864929	0.714893	0.506599	0.039*
H6B	0.965074	0.725639	0.659402	0.039*
C7	0.7975 (16)	0.8732 (15)	0.6540 (9)	0.0309 (18)
H7A	0.653666	0.832240	0.633311	0.037*
H7B	0.879991	0.989880	0.594356	0.037*
C8	0.8430 (14)	0.9360 (14)	0.8119 (9)	0.0262 (16)
H8A	0.988852	0.985256	0.831092	0.031*
H8B	0.814767	1.047758	0.828919	0.031*
C9	0.7226 (14)	0.7718 (14)	0.9176 (8)	0.0257 (16)
H9A	0.772439	0.673575	0.917303	0.031*
H9B	0.743231	0.829398	1.014935	0.031*
C10	0.5016 (13)	0.6699 (13)	0.8799 (8)	0.0222 (15)
Se11	0.31509 (15)	0.73496 (15)	0.95420 (9)	0.0304 (3)
N12	0.1178 (13)	0.5308 (14)	0.8370 (9)	0.0327 (16)
N13	0.1976 (12)	0.4468 (13)	0.7656 (8)	0.0277 (15)
C14	0.4026 (13)	0.5159 (14)	0.7841 (8)	0.0233 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se1	0.0262 (5)	0.0322 (5)	0.0348 (5)	0.0169 (4)	0.0023 (4)	−0.0034 (4)
N2	0.034 (5)	0.028 (4)	0.035 (4)	0.013 (4)	0.011 (3)	0.004 (3)
N3	0.033 (4)	0.026 (4)	0.027 (3)	0.011 (4)	0.005 (3)	0.000 (3)
C4	0.023 (4)	0.023 (4)	0.019 (3)	0.010 (3)	−0.002 (3)	−0.002 (3)
C5	0.021 (4)	0.029 (4)	0.023 (3)	0.012 (4)	0.001 (3)	−0.002 (3)
C6	0.030 (5)	0.033 (5)	0.032 (4)	0.014 (4)	0.009 (4)	−0.001 (4)
C7	0.031 (5)	0.032 (5)	0.028 (4)	0.014 (4)	0.005 (3)	0.004 (3)
C8	0.023 (4)	0.025 (4)	0.026 (3)	0.007 (4)	0.002 (3)	−0.004 (3)
C9	0.020 (4)	0.031 (4)	0.020 (3)	0.008 (4)	0.003 (3)	−0.002 (3)
C10	0.022 (4)	0.022 (4)	0.021 (3)	0.009 (3)	0.004 (3)	−0.001 (3)
Se11	0.0275 (5)	0.0315 (5)	0.0321 (5)	0.0138 (4)	0.0066 (4)	−0.0050 (4)
N12	0.021 (4)	0.038 (5)	0.036 (4)	0.012 (4)	0.002 (3)	−0.003 (3)
N13	0.019 (4)	0.034 (4)	0.027 (3)	0.011 (3)	0.003 (3)	0.001 (3)
C14	0.021 (4)	0.028 (4)	0.020 (3)	0.011 (4)	0.001 (3)	0.000 (3)

Geometric parameters (Å, º)

Se1—C5	1.837 (9)	C7—H7B	0.9900
Se1—N2	1.879 (9)	C8—C9	1.526 (12)
N2—N3	1.269 (11)	C8—H8A	0.9900
N3—C4	1.383 (12)	C8—H8B	0.9900
C4—C5	1.378 (13)	C9—C10	1.499 (12)
C4—C14	1.473 (11)	C9—H9A	0.9900
C5—C6	1.509 (14)	C9—H9B	0.9900
C6—C7	1.529 (13)	C10—C14	1.376 (12)
C6—H6A	0.9900	C10—Se11	1.845 (8)
C6—H6B	0.9900	Se11—N12	1.895 (9)
C7—C8	1.538 (12)	N12—N13	1.267 (11)
C7—H7A	0.9900	N13—C14	1.381 (11)
C5—Se1—N2	87.9 (4)	C9—C8—C7	114.7 (8)
N3—N2—Se1	110.2 (7)	C9—C8—H8A	108.6
N2—N3—C4	117.8 (8)	C7—C8—H8A	108.6
C5—C4—N3	115.8 (8)	C9—C8—H8B	108.6
C5—C4—C14	128.7 (8)	C7—C8—H8B	108.6
N3—C4—C14	115.5 (8)	H8A—C8—H8B	107.6
C4—C5—C6	133.7 (8)	C10—C9—C8	111.1 (6)
C4—C5—Se1	108.3 (7)	C10—C9—H9A	109.4
C6—C5—Se1	118.0 (6)	C8—C9—H9A	109.4
C5—C6—C7	118.1 (8)	C10—C9—H9B	109.4
C5—C6—H6A	107.8	C8—C9—H9B	109.4
C7—C6—H6A	107.8	H9A—C9—H9B	108.0
C5—C6—H6B	107.8	C14—C10—C9	126.9 (8)
C7—C6—H6B	107.8	C14—C10—Se11	108.1 (6)
H6A—C6—H6B	107.1	C9—C10—Se11	125.0 (6)
C6—C7—C8	114.7 (7)	C10—Se11—N12	87.4 (4)
C6—C7—H7A	108.6	N13—N12—Se11	110.3 (6)
C8—C7—H7A	108.6	N12—N13—C14	117.5 (8)
C6—C7—H7B	108.6	C10—C14—N13	116.6 (8)
C8—C7—H7B	108.6	C10—C14—C4	124.8 (8)
H7A—C7—H7B	107.6	N13—C14—C4	118.5 (8)
C5—Se1—N2—N3	0.2 (6)	C8—C9—C10—Se11	−94.1 (8)
Se1—N2—N3—C4	0.1 (9)	C14—C10—Se11—N12	0.0 (6)
N2—N3—C4—C5	−0.5 (11)	C9—C10—Se11—N12	179.1 (7)
N2—N3—C4—C14	−178.9 (7)	C10—Se11—N12—N13	0.2 (6)
N3—C4—C5—C6	179.1 (8)	Se11—N12—N13—C14	−0.4 (10)
C14—C4—C5—C6	−2.7 (14)	C9—C10—C14—N13	−179.3 (7)
N3—C4—C5—Se1	0.6 (8)	Se11—C10—C14—N13	−0.2 (9)
C14—C4—C5—Se1	178.8 (6)	C9—C10—C14—C4	4.8 (13)
N2—Se1—C5—C4	−0.4 (6)	Se11—C10—C14—C4	−176.1 (6)
N2—Se1—C5—C6	−179.2 (7)	N12—N13—C14—C10	0.4 (11)
C4—C5—C6—C7	−5.1 (14)	N12—N13—C14—C4	176.6 (7)

Se1—C5—C6—C7	173.2 (6)	C5—C4—C14—C10	−46.0 (12)
C5—C6—C7—C8	82.6 (11)	N3—C4—C14—C10	132.3 (9)
C6—C7—C8—C9	−59.7 (11)	C5—C4—C14—N13	138.2 (8)
C7—C8—C9—C10	−49.6 (10)	N3—C4—C14—N13	−43.6 (10)
C8—C9—C10—C14	84.9 (10)		