

rac-12-Selena-13,14-diazatricyclo[9.3.0.0^{2,4}]tetradeca-11,13-diene

Heiner Detert* and Dieter Schollmeyer

Johannes Gutenberg University Mainz, Department of Chemistry, Duesbergweg 10-14, 55099 Mainz, Germany.

*Correspondence e-mail: detert@uni-mainz.de

Received 17 July 2020

Accepted 4 August 2020

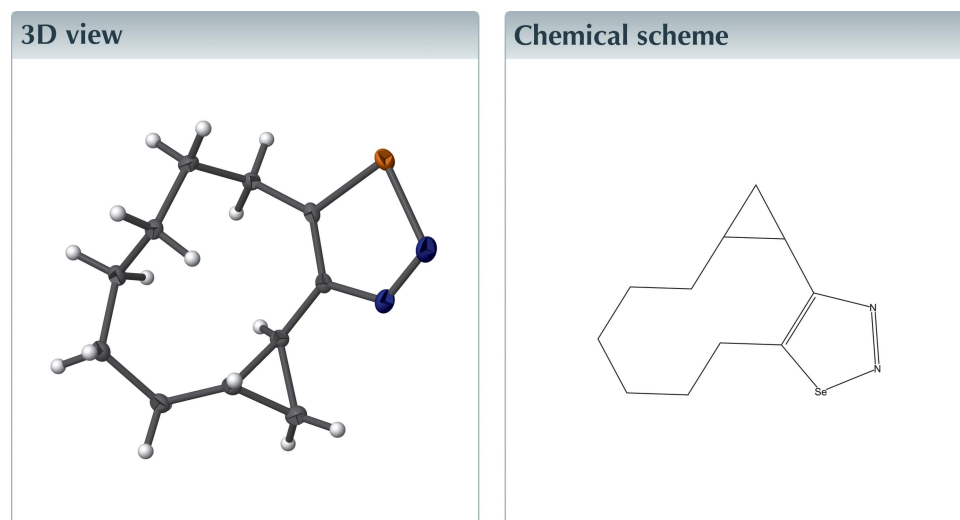
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

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

CCDC reference: 2021398

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

The centrosymmetric crystal structure of the title compound, C₁₁H₁₆N₂Se, is built up from alternating strands of (*R,R*)- and (*S,S*)-enantiomers. These strands, which propagate along the *c*-axis direction, are composed of homochiral molecules related to each other by twofold screw axes. The shape of the molecule is an almost planar unit around the selenadiazole ring with a hexamethylene chain as an arched handle.



Structure description

1,2,3-Selenadiazoles are synthesized from SeO₂-oxidation 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).

The arbitrarily chosen asymmetric molecule of the title compound (Fig. 1) has *S* configurations for atoms C5 and C6 but crystal symmetry generates a racemic mixture. The selenadiazole ring with the directly bound carbon atoms and one bond of the cyclopropane ring is almost planar, with a maximum deviation from this plane of 0.037 (2) Å at C12 and the dihedral angle between the selenadiazole ring and the cyclopropane ring is 69.0 (2)°. Though the carbocyclic part is of medium ring size, the hexamethylene tether appears to be free of Pitzer and Prelog strain.

No directional interactions beyond normal van der Waals contacts could be identified in the crystal. The packing consists of strands of homochiral molecules, related to each other by twofold screw axes, propagating along the *c*-axis direction. The (*R,R*)- and (*S,S*)-enantiomers alternate along the *a*-axis direction, being related by crystallographic *c*-glides (Fig. 2).

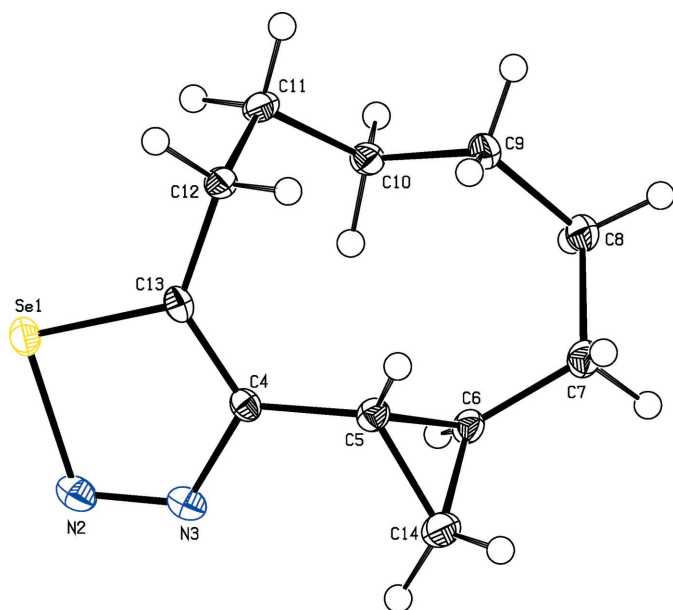


Figure 1
Perspective view of the title compound with displacement ellipsoids drawn at the 50% probability level.

Synthesis and crystallization

The title compound was prepared in ten steps from cyclooctene according to Moore & Ward (1963), Moore & Bertelson (1962), Gardner & Narayana (1961), Detert & Meier (1997) and Whitham & Zaidlewicz (1972). Recrystallization from petroleum ether gave slightly pinkish crystals with m.p. 369 K.

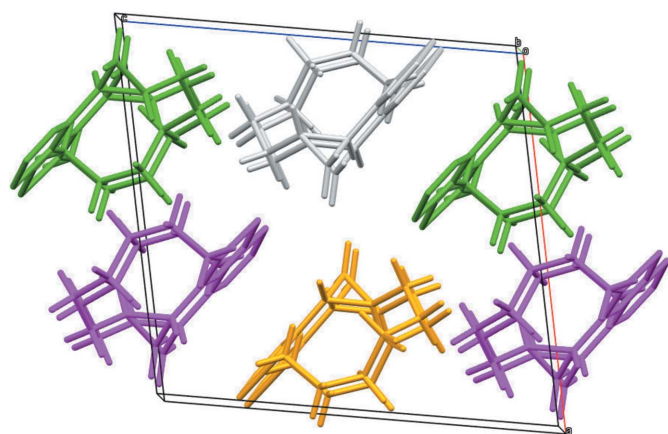


Figure 2
Packing diagram of the title compound viewed along the *b*-axis direction. Colour key: the asymmetric molecule and its translation clones along [010] grey; molecules generated by twofold screw axes green; molecules generated by inversion symmetry orange; molecules generated by *c*-glides purple.

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₁₁ H ₁₆ N ₂ Se
<i>M_r</i>	255.22
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.0239 (6), 7.1317 (3), 12.6836 (7)
β (°)	101.104 (4)
<i>V</i> (Å ³)	1067.27 (9)
<i>Z</i>	4
Radiation type	Mo Kα
μ (mm ⁻¹)	3.48
Crystal size (mm)	0.55 × 0.47 × 0.10
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Integration
<i>T</i> _{min} , <i>T</i> _{max}	0.228, 0.704
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	5541, 2570, 2364
<i>R</i> _{int}	0.021
(sin θ/λ) _{max} (Å ⁻¹)	0.661
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.097, 1.10
No. of reflections	2570
No. of parameters	127
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.13, -0.90

Computer programs: *X-AREA* WinXpose, *Recipe* and *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.

References

- Al-Smadi, M. & Ratrou, S. (2004). *Molecules*, **9**, 957–967.
- Bissingner, H.-J., Detert, H. & Meier, H. (1988). *Liebigs Ann. Chem.* pp. 221–224.
- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
- Detert, H. (2011). *Targets in Heterocyclic Systems*, **15**, 1–49.
- Detert, H. & Meier, H. (1997). *Liebigs Ann. Recl.* pp. 1557–1563.
- Gardner, P. D. & Narayana, M. (1961). *J. Org. Chem.* **26**, 3518–3519.
- Meier, H. (1972). *Synthesis*, pp. 235–253.
- Moore, W. R. & Bertelson, R. C. (1962). *J. Org. Chem.* **27**, 4182–4186.
- Moore, W. R. & Ward, H. R. (1963). *J. Am. Chem. Soc.* **85**, 1, 86–89.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Stoe & Cie (2019). *X-RED* and *X-AREA*. Stoe & Cie, Darmstadt, Germany.
- Whitham, G. H. & Zaidlewicz, M. (1972). *J. Chem. Soc. Perkin Trans. I*, pp. 1509–1513.
- Yalpani, M., Lalezari, I. & Shafiee, A. (1971). *J. Org. Chem.* **36**, 2836–2838.

full crystallographic data

IUCrData (2020). 5, x201081 [https://doi.org/10.1107/S2414314620010810]

***rac*-12-Selena-13,14-diazatricyclo[9.3.0.0^{2,4}]tetradeca-11,13-diene**

Heiner Detert and Dieter Schollmeyer

rac*-12-Selena-13,14-diazatricyclo[9.3.0.0^{2,4}]tetradeca-11,13-dieneCrystal data*

$C_{11}H_{16}N_2Se$	$F(000) = 520$
$M_r = 255.22$	$D_x = 1.588 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 12.0239 (6) \text{ \AA}$	Cell parameters from 11220 reflections
$b = 7.1317 (3) \text{ \AA}$	$\theta = 2.9\text{--}28.5^\circ$
$c = 12.6836 (7) \text{ \AA}$	$\mu = 3.48 \text{ mm}^{-1}$
$\beta = 101.104 (4)^\circ$	$T = 120 \text{ K}$
$V = 1067.27 (9) \text{ \AA}^3$	Plate, colourless
$Z = 4$	$0.55 \times 0.47 \times 0.10 \text{ mm}$

Data collection

Stoe IPDS 2T	5541 measured reflections
diffractometer	2570 independent reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	2364 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	$R_{\text{int}} = 0.021$
rotation method, ω scans	$\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 3.3^\circ$
Absorption correction: integration	$h = -15 \rightarrow 15$
$T_{\text{min}} = 0.228$, $T_{\text{max}} = 0.704$	$k = -9 \rightarrow 9$
	$l = -15 \rightarrow 16$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 1.4452P]$
$wR(F^2) = 0.097$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2570 reflections	$\Delta\rho_{\text{max}} = 1.13 \text{ e \AA}^{-3}$
127 parameters	$\Delta\rho_{\text{min}} = -0.90 \text{ e \AA}^{-3}$
0 restraints	
Primary atom site location: dual	

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. Hydrogen atoms attached to carbon atoms were placed at calculated positions and were refined in the riding-model approximation with C—H = 0.95 \AA and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Se1	0.01806 (2)	0.53889 (3)	0.19801 (2)	0.01717 (11)
N2	0.08518 (19)	0.7735 (3)	0.24245 (18)	0.0195 (4)
N3	0.16960 (17)	0.7494 (3)	0.31890 (17)	0.0167 (4)
C4	0.1961 (2)	0.5686 (3)	0.35355 (19)	0.0131 (4)
C5	0.2954 (2)	0.5360 (3)	0.4406 (2)	0.0144 (4)
H5	0.337544	0.417298	0.433140	0.017*
C6	0.2942 (2)	0.5921 (3)	0.55614 (18)	0.0149 (4)
H6	0.225279	0.662016	0.567102	0.018*
C7	0.3456 (2)	0.4626 (3)	0.6468 (2)	0.0177 (5)
H7A	0.375621	0.539411	0.711012	0.021*
H7B	0.410401	0.396039	0.626172	0.021*
C8	0.2633 (2)	0.3164 (4)	0.67731 (19)	0.0178 (5)
H8A	0.203057	0.382731	0.705866	0.021*
H8B	0.305015	0.236704	0.735703	0.021*
C9	0.2071 (2)	0.1890 (3)	0.58429 (19)	0.0173 (5)
H9A	0.260533	0.170100	0.534790	0.021*
H9B	0.192121	0.064881	0.613659	0.021*
C10	0.09558 (19)	0.2684 (3)	0.52058 (18)	0.0154 (4)
H10A	0.035621	0.252598	0.563508	0.018*
H10B	0.105037	0.404482	0.509630	0.018*
C11	0.0569 (2)	0.1748 (3)	0.41110 (19)	0.0170 (5)
H11A	-0.022326	0.212211	0.382070	0.020*
H11B	0.058059	0.037076	0.421121	0.020*
C12	0.1307 (2)	0.2250 (3)	0.32802 (19)	0.0147 (4)
H12A	0.210110	0.187617	0.356552	0.018*
H12B	0.103796	0.153162	0.261179	0.018*
C13	0.1270 (2)	0.4310 (3)	0.30231 (19)	0.0143 (4)
C14	0.3690 (2)	0.6950 (4)	0.4927 (2)	0.0195 (5)
H14A	0.451685	0.673076	0.511923	0.023*
H14B	0.346890	0.824166	0.468684	0.023*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se1	0.01788 (15)	0.01843 (16)	0.01400 (15)	0.00192 (8)	0.00010 (10)	0.00198 (8)
N2	0.0245 (10)	0.0147 (9)	0.0200 (11)	0.0019 (8)	0.0059 (8)	0.0027 (8)
N3	0.0199 (10)	0.0135 (9)	0.0180 (10)	0.0013 (8)	0.0068 (8)	0.0017 (7)
C4	0.0150 (10)	0.0136 (9)	0.0112 (10)	0.0013 (8)	0.0038 (8)	0.0011 (8)
C5	0.0148 (10)	0.0156 (11)	0.0130 (11)	-0.0013 (8)	0.0034 (9)	-0.0015 (8)
C6	0.0164 (10)	0.0163 (10)	0.0117 (10)	-0.0020 (9)	0.0021 (8)	-0.0022 (8)
C7	0.0177 (11)	0.0213 (12)	0.0135 (11)	-0.0028 (9)	0.0017 (9)	-0.0002 (8)
C8	0.0199 (11)	0.0200 (11)	0.0130 (11)	-0.0020 (9)	0.0021 (9)	0.0013 (9)
C9	0.0218 (11)	0.0166 (10)	0.0128 (11)	-0.0008 (9)	0.0013 (9)	0.0013 (8)
C10	0.0170 (10)	0.0162 (10)	0.0136 (11)	-0.0025 (8)	0.0044 (9)	0.0010 (8)
C11	0.0184 (11)	0.0157 (10)	0.0166 (11)	-0.0058 (9)	0.0027 (9)	-0.0015 (9)

C12	0.0176 (10)	0.0127 (10)	0.0134 (10)	-0.0011 (8)	0.0022 (8)	-0.0013 (8)
C13	0.0154 (10)	0.0166 (10)	0.0109 (10)	0.0020 (9)	0.0027 (8)	0.0024 (8)
C14	0.0211 (11)	0.0197 (11)	0.0179 (12)	-0.0054 (10)	0.0040 (9)	-0.0016 (9)

Geometric parameters (Å, °)

Se1—C13	1.841 (2)	C8—H8A	0.9900
Se1—N2	1.896 (2)	C8—H8B	0.9900
N2—N3	1.273 (3)	C9—C10	1.535 (3)
N3—C4	1.379 (3)	C9—H9A	0.9900
C4—C13	1.367 (3)	C9—H9B	0.9900
C4—C5	1.480 (3)	C10—C11	1.530 (3)
C5—C14	1.510 (3)	C10—H10A	0.9900
C5—C6	1.522 (3)	C10—H10B	0.9900
C5—H5	1.0000	C11—C12	1.544 (3)
C6—C14	1.507 (3)	C11—H11A	0.9900
C6—C7	1.511 (3)	C11—H11B	0.9900
C6—H6	1.0000	C12—C13	1.504 (3)
C7—C8	1.538 (3)	C12—H12A	0.9900
C7—H7A	0.9900	C12—H12B	0.9900
C7—H7B	0.9900	C14—H14A	0.9900
C8—C9	1.538 (3)	C14—H14B	0.9900
C13—Se1—N2	87.26 (10)	C8—C9—H9A	108.9
N3—N2—Se1	109.79 (16)	C10—C9—H9B	108.9
N2—N3—C4	118.1 (2)	C8—C9—H9B	108.9
C13—C4—N3	115.9 (2)	H9A—C9—H9B	107.7
C13—C4—C5	124.8 (2)	C11—C10—C9	113.5 (2)
N3—C4—C5	119.3 (2)	C11—C10—H10A	108.9
C4—C5—C14	121.9 (2)	C9—C10—H10A	108.9
C4—C5—C6	121.4 (2)	C11—C10—H10B	108.9
C14—C5—C6	59.64 (15)	C9—C10—H10B	108.9
C4—C5—H5	114.4	H10A—C10—H10B	107.7
C14—C5—H5	114.4	C10—C11—C12	113.84 (19)
C6—C5—H5	114.4	C10—C11—H11A	108.8
C14—C6—C7	120.4 (2)	C12—C11—H11A	108.8
C14—C6—C5	59.79 (15)	C10—C11—H11B	108.8
C7—C6—C5	119.6 (2)	C12—C11—H11B	108.8
C14—C6—H6	115.3	H11A—C11—H11B	107.7
C7—C6—H6	115.3	C13—C12—C11	112.17 (19)
C5—C6—H6	115.3	C13—C12—H12A	109.2
C6—C7—C8	114.7 (2)	C11—C12—H12A	109.2
C6—C7—H7A	108.6	C13—C12—H12B	109.2
C8—C7—H7A	108.6	C11—C12—H12B	109.2
C6—C7—H7B	108.6	H12A—C12—H12B	107.9
C8—C7—H7B	108.6	C4—C13—C12	127.5 (2)
H7A—C7—H7B	107.6	C4—C13—Se1	108.95 (17)
C7—C8—C9	114.6 (2)	C12—C13—Se1	123.47 (18)

C7—C8—H8A	108.6	C6—C14—C5	60.58 (15)
C9—C8—H8A	108.6	C6—C14—H14A	117.7
C7—C8—H8B	108.6	C5—C14—H14A	117.7
C9—C8—H8B	108.6	C6—C14—H14B	117.7
H8A—C8—H8B	107.6	C5—C14—H14B	117.7
C10—C9—C8	113.3 (2)	H14A—C14—H14B	114.8
C10—C9—H9A	108.9		
C13—Se1—N2—N3	0.23 (17)	C7—C8—C9—C10	-89.4 (3)
Se1—N2—N3—C4	0.2 (3)	C8—C9—C10—C11	163.53 (19)
N2—N3—C4—C13	-0.8 (3)	C9—C10—C11—C12	-70.9 (3)
N2—N3—C4—C5	178.6 (2)	C10—C11—C12—C13	-62.5 (3)
C13—C4—C5—C14	179.2 (2)	N3—C4—C13—C12	-175.5 (2)
N3—C4—C5—C14	-0.1 (3)	C5—C4—C13—C12	5.1 (4)
C13—C4—C5—C6	-109.3 (3)	N3—C4—C13—Se1	0.9 (3)
N3—C4—C5—C6	71.3 (3)	C5—C4—C13—Se1	-178.47 (18)
C4—C5—C6—C14	-111.1 (2)	C11—C12—C13—C4	89.1 (3)
C4—C5—C6—C7	138.9 (2)	C11—C12—C13—Se1	-86.8 (2)
C14—C5—C6—C7	-110.0 (2)	N2—Se1—C13—C4	-0.62 (17)
C14—C6—C7—C8	-159.1 (2)	N2—Se1—C13—C12	175.9 (2)
C5—C6—C7—C8	-88.8 (3)	C7—C6—C14—C5	108.7 (2)
C6—C7—C8—C9	56.9 (3)	C4—C5—C14—C6	110.3 (2)
