

# (10*Z*)-4*H*,5*H*,6*H*,7*H*,8*H*,9*H*-Cyclodeca[*d*][1,2,3]-selenadiazole

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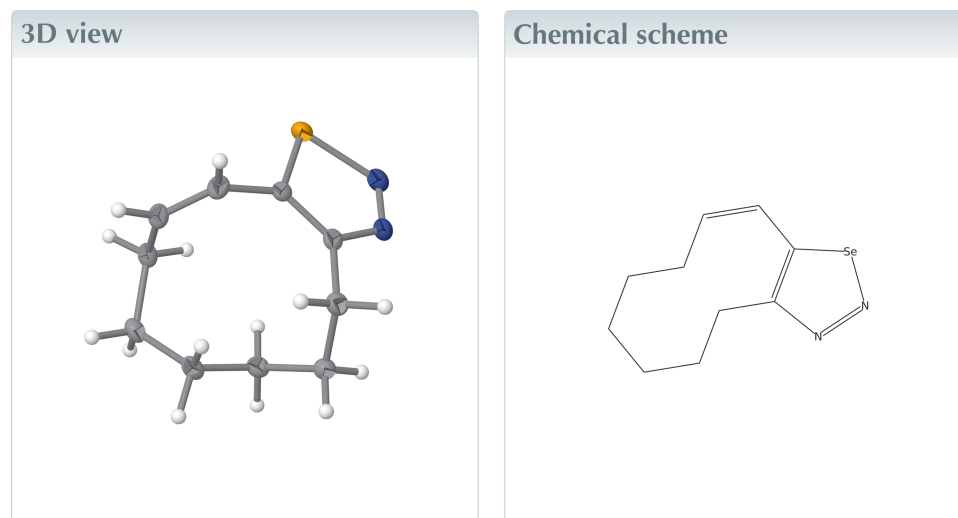
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**Keywords:** crystal structure; heterocycle; medium-sized ring; selenium.**CCDC reference:** 2402782**Structural data:** full structural data are available from iucrdata.iucr.org

The title compound, C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>Se, was prepared from a semicarbazone and selenium dioxide. The planes of the heterocycle and the *cis* double bond are almost mutually orthogonal and the hexamethylene tether is nearly strain-free.

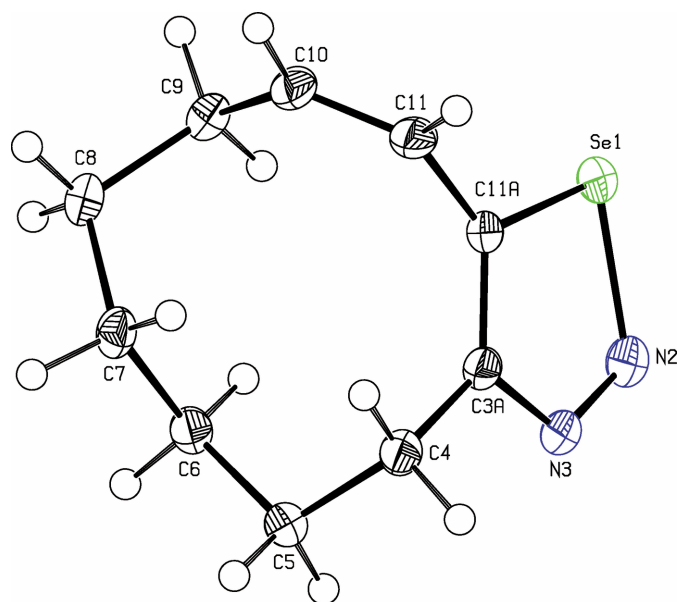


## Structure description

The title compound, C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>Se (Fig. 1), was prepared as part of a project focusing on medium-sized cycloalkynes (Bissinger *et al.*, 1988; Detert & Meier, 1997). Thermolysis of 1,2,3-selenadiazoles is an advantageous route to strained cycloalkynes. They are prepared by oxidation of semicarbazones with selenium dioxide (Lalezari *et al.*, 1972). Selenious acid oxidized *Z*-cyclodec-3-enone semicarbazone to a mixture of the title compound (63%) and the homoconjugated (5*Z*)-isomer. In the crystal, the molecules are arranged in layers parallel to the *ac* plane. Within a layer, all molecules adopt the same orientation, while in the neighbouring layers, the orientation of the molecules is inverted. The selenadiazole ring is essentially planar with an r.m.s. deviation of 0.002 (2) Å. In addition, the connecting atoms of the aliphatic tether are coplanar, C4 lies only 0.044 (2) Å above and C11 – 0.012 (2) Å below the selenadiazole plane. A negligible torsion angle [0.02 (4)°] twists the double bond (C10=C11) but the dihedral angle of 88.56 (15)° between the heterocycle and *cis*-olefin disrupts the  $\pi$ -conjugation. The hexamethylene chain shows a strain-free staggered arrangement. The packing is shown in Fig. 2.

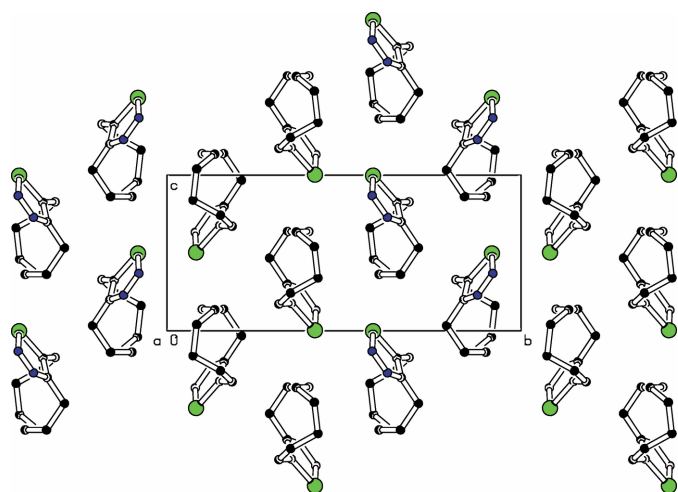
## Synthesis and crystallization

The title compound was prepared in 63% yield from the semicarbazone of (3*Z*)-cyclodecenone. The required ketone appeared in 10% yield upon selenious acid catalyzed hydrolysis/isomerization of (2*Z*)-cyclodecenone semicarbazone (Whitham & Zaidlewicz, 1972; Hirano *et al.*, 1974). Selenium dioxide (2 mmol) was added to 0.5 mmol of the semicarbazone in 10 ml of 1,4-dioxane. After 3 days stirring, the solvent was evaporated,



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

the slurry was mixed with toluene, washed with water, dried ( $\text{MgSO}_4$ ) and the compound isolated *via* chromatography with toluene/ethyl acetate on silica gel. Yield: 63% of yellowish crystals with the typical fetid odor of selenadiazoles. NMR analysis at 298 K gave clear signals for the olefinic subunit but broad signals for the methylene chain, indicating constricted conformational interconversions on the NMR time scale. Only at very low temperatures did the diastereotopic protons *e.g.* at C-4 gave separate signals of good resolution. M.p. = 315 K.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 293 K): 6.27 (*d*, 1 H,  $J = 11$  Hz, H—C-11), 5.88 (*ddd*, 1 H,  $J = J' = 11$  Hz,  $J'' = 5.5$  Hz, H—C-10), 3.05 (*bs*, 2 H), 2.96 (*bs*, 2 H), 1.74 (*bs*, 2 H), 1.48 (*m*, 4 H), 0.99 (*bs*, 2 H); (400 MHz,  $\text{CDCl}_3$ , 228 K): ; (400 MHz,  $\text{CDCl}_3$ ,



**Figure 2**  
Part of the packing diagram. View along the *a* axis.

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{10}\text{H}_{14}\text{N}_2\text{Se}$
$M_r$	241.19
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	120
$a, b, c$ (Å)	7.9646 (6), 17.0830 (15), 8.0572 (6)
$\beta$ (°)	111.425 (6)
$V$ (Å <sup>3</sup> )	1020.50 (15)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	3.64
Crystal size (mm)	0.29 × 0.21 × 0.11
Data collection	
Diffractometer	Stoe <i>IPDS</i> 2T
Absorption correction	Integration [ <i>X-RED32</i> (Stoe & Cie, 2020), absorption correction by Gaussian integration (Coppens, 1970)]
$T_{\min}, T_{\max}$	0.381, 0.697
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	5508, 2430, 2093
$R_{\text{int}}$	0.020
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.658
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.030, 0.067, 1.12
No. of reflections	2430
No. of parameters	118
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.41, -0.40

Computer programs: *X-AREA WinXpose, Recipe* and *Integrate* (Stoe & Cie, 2020), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b) and *PLATON* (Spek, 2020).

228 K): 6.25 (*d*, 1 H,  $J = 11$  Hz, H—C-11), 5.85 (*ddd*, 1 H,  $J = J' = 11$  Hz,  $J'' = 5.5$  Hz, HC-10), 3.18 (pseudo-*d*, 1 H,  $J = 14$  Hz, H—CH-4), 2.78 (*ddd*,  $J = J' = 14$  Hz,  $J'' = 4$  Hz, HC—H-4), 1.95 (*m*, 3 H), 1.56 (*t*,  $J = 13$  Hz), 1.42 (*m*, 1 H), 1.25 (*m*, 4 H), 0.58 (*m*, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 159.5 ( $^2\text{JC—Se} = 32$  Hz, C-3a), 155.1 ( $^1\text{JC—Se} = 130$  Hz, C-11a), 138.9 ( $^2\text{JC—Se} = 37$  Hz, C-11), 119.9 (C-10), 26.8, 25.6, 24.9, 24.7, 20.9, 20.5 (C4 - C9).  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ): 221.2 UV-Vis (EtOH): 224 (2.93), 239 (3.49), 294 (3.41) nm (log $\epsilon$ ) IR ( $\text{CDCl}_3$ ): 3005, 2920, 2840, 1495, 1430, 1310, 1255, 1210  $\text{cm}^{-1}$ .

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

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## full crystallographic data

*IUCrData* (2024). **9**, x241107 [<https://doi.org/10.1107/S2414314624011076>]

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*Crystal data*

$C_{10}H_{14}N_2Se$	$D_x = 1.570 \text{ Mg m}^{-3}$
$M_r = 241.19$	Melting point: 315 K
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 7.9646 (6) \text{ \AA}$	Cell parameters from 10316 reflections
$b = 17.0830 (15) \text{ \AA}$	$\theta = 2.4\text{--}28.4^\circ$
$c = 8.0572 (6) \text{ \AA}$	$\mu = 3.64 \text{ mm}^{-1}$
$\beta = 111.425 (6)^\circ$	$T = 120 \text{ K}$
$V = 1020.50 (15) \text{ \AA}^3$	Block, colorless
$Z = 4$	$0.29 \times 0.21 \times 0.11 \text{ mm}$
$F(000) = 488$	

*Data collection*

Stoe IPDS 2T	$T_{\min} = 0.381, T_{\max} = 0.697$
diffractometer	5508 measured reflections
Radiation source: sealed X-ray tube, 12x0.4mm	2430 independent reflections
long-fine focus	2093 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels $\text{mm}^{-1}$	$R_{\text{int}} = 0.020$
rotation method, $\omega$ scans	$\theta_{\max} = 27.9^\circ, \theta_{\min} = 2.4^\circ$
Absorption correction: integration	$h = -7 \rightarrow 10$
[X-Red32 (Stoe & Cie, 2020), absorption	$k = -21 \rightarrow 22$
correction by Gaussian integration (Coppens,	$l = -10 \rightarrow 10$
1970)]	

*Refinement*

Refinement on $F^2$	Hydrogen site location: inferred from
Least-squares matrix: full	neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	H-atom parameters constrained
$wR(F^2) = 0.067$	$w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 1.2555P]$
$S = 1.12$	where $P = (F_o^2 + 2F_c^2)/3$
2430 reflections	$(\Delta/\sigma)_{\max} < 0.001$
118 parameters	$\Delta\rho_{\max} = 0.41 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.40 \text{ e \AA}^{-3}$
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 were placed at calculated positions and were refined in the riding-model approximation with  $C_{\text{aromatic}}\text{-H} = 0.95 \text{ \AA}$  or  $C_{\text{methylene}}\text{-H} = 0.99 \text{ \AA}$  and with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ .

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Se1	0.22155 (3)	0.41792 (2)	0.00291 (3)	0.02588 (8)
N2	0.0679 (3)	0.42034 (14)	0.1321 (3)	0.0287 (5)
N3	0.1303 (3)	0.37734 (13)	0.2705 (3)	0.0242 (4)
C3A	0.2906 (3)	0.33871 (13)	0.3010 (3)	0.0200 (4)
C4	0.3665 (3)	0.29010 (14)	0.4674 (3)	0.0223 (5)
H4A	0.467261	0.257977	0.460615	0.027*
H4B	0.271954	0.254034	0.474213	0.027*
C5	0.4350 (3)	0.34033 (14)	0.6375 (3)	0.0227 (5)
H5A	0.331482	0.368148	0.650443	0.027*
H5B	0.486911	0.305438	0.741913	0.027*
C6	0.5776 (3)	0.40050 (14)	0.6379 (3)	0.0223 (5)
H6A	0.525551	0.434969	0.532727	0.027*
H6B	0.606410	0.433562	0.745666	0.027*
C7	0.7529 (3)	0.36533 (14)	0.6347 (3)	0.0231 (5)
H7A	0.836267	0.356584	0.758932	0.028*
H7B	0.725966	0.313698	0.574953	0.028*
C8	0.8476 (3)	0.41614 (15)	0.5396 (3)	0.0235 (5)
H8A	0.965934	0.392425	0.555708	0.028*
H8B	0.870326	0.468471	0.596223	0.028*
C9	0.7400 (3)	0.42610 (13)	0.3392 (3)	0.0217 (5)
H9A	0.626221	0.454180	0.322631	0.026*
H9B	0.810602	0.458548	0.286372	0.026*
C10	0.6965 (3)	0.34927 (15)	0.2428 (3)	0.0233 (5)
H10	0.794761	0.321303	0.231365	0.028*
C11	0.5350 (3)	0.31628 (15)	0.1718 (3)	0.0235 (5)
H11	0.527227	0.267070	0.114513	0.028*
C11A	0.3666 (3)	0.35080 (14)	0.1757 (3)	0.0200 (4)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Se1	0.01898 (12)	0.03822 (15)	0.01753 (12)	−0.00109 (10)	0.00322 (8)	0.00338 (10)
N2	0.0176 (9)	0.0410 (13)	0.0244 (10)	0.0014 (9)	0.0042 (8)	0.0008 (9)
N3	0.0153 (9)	0.0351 (12)	0.0216 (10)	−0.0003 (8)	0.0059 (8)	−0.0011 (8)
C3A	0.0165 (10)	0.0235 (12)	0.0198 (10)	−0.0040 (8)	0.0063 (8)	−0.0041 (9)
C4	0.0195 (11)	0.0246 (11)	0.0217 (11)	−0.0025 (9)	0.0061 (9)	0.0008 (9)
C5	0.0205 (11)	0.0279 (12)	0.0190 (11)	−0.0006 (9)	0.0063 (9)	0.0010 (9)
C6	0.0211 (11)	0.0243 (12)	0.0198 (11)	−0.0008 (9)	0.0054 (9)	−0.0015 (9)
C7	0.0169 (10)	0.0248 (12)	0.0232 (11)	0.0006 (9)	0.0021 (9)	0.0037 (9)
C8	0.0163 (10)	0.0250 (11)	0.0257 (11)	−0.0027 (9)	0.0035 (9)	−0.0019 (10)
C9	0.0168 (10)	0.0214 (12)	0.0264 (11)	−0.0005 (8)	0.0073 (9)	0.0014 (9)
C10	0.0180 (10)	0.0284 (12)	0.0256 (11)	0.0011 (9)	0.0105 (9)	−0.0028 (9)

C11	0.0229 (11)	0.0277 (12)	0.0229 (11)	-0.0014 (9)	0.0121 (9)	-0.0053 (9)
C11A	0.0168 (10)	0.0255 (12)	0.0164 (10)	-0.0046 (8)	0.0048 (8)	-0.0034 (9)

*Geometric parameters (Å, °)*

Se1—C11A	1.847 (2)	C6—H6B	0.9900
Se1—N2	1.875 (2)	C7—C8	1.527 (3)
N2—N3	1.274 (3)	C7—H7A	0.9900
N3—C3A	1.377 (3)	C7—H7B	0.9900
C3A—C11A	1.370 (3)	C8—C9	1.536 (3)
C3A—C4	1.503 (3)	C8—H8A	0.9900
C4—C5	1.538 (3)	C8—H8B	0.9900
C4—H4A	0.9900	C9—C10	1.500 (3)
C4—H4B	0.9900	C9—H9A	0.9900
C5—C6	1.531 (3)	C9—H9B	0.9900
C5—H5A	0.9900	C10—C11	1.327 (3)
C5—H5B	0.9900	C10—H10	0.9500
C6—C7	1.529 (3)	C11—C11A	1.475 (3)
C6—H6A	0.9900	C11—H11	0.9500
C11A—Se1—N2	87.18 (9)	C6—C7—H7A	108.8
N3—N2—Se1	110.36 (16)	C8—C7—H7B	108.8
N2—N3—C3A	118.2 (2)	C6—C7—H7B	108.8
C11A—C3A—N3	115.3 (2)	H7A—C7—H7B	107.6
C11A—C3A—C4	126.8 (2)	C7—C8—C9	113.71 (19)
N3—C3A—C4	117.9 (2)	C7—C8—H8A	108.8
C3A—C4—C5	112.50 (19)	C9—C8—H8A	108.8
C3A—C4—H4A	109.1	C7—C8—H8B	108.8
C5—C4—H4A	109.1	C9—C8—H8B	108.8
C3A—C4—H4B	109.1	H8A—C8—H8B	107.7
C5—C4—H4B	109.1	C10—C9—C8	112.46 (19)
H4A—C4—H4B	107.8	C10—C9—H9A	109.1
C6—C5—C4	113.46 (19)	C8—C9—H9A	109.1
C6—C5—H5A	108.9	C10—C9—H9B	109.1
C4—C5—H5A	108.9	C8—C9—H9B	109.1
C6—C5—H5B	108.9	H9A—C9—H9B	107.8
C4—C5—H5B	108.9	C11—C10—C9	126.8 (2)
H5A—C5—H5B	107.7	C11—C10—H10	116.6
C7—C6—C5	114.7 (2)	C9—C10—H10	116.6
C7—C6—H6A	108.6	C10—C11—C11A	124.5 (2)
C5—C6—H6A	108.6	C10—C11—H11	117.8
C7—C6—H6B	108.6	C11A—C11—H11	117.8
C5—C6—H6B	108.6	C3A—C11A—C11	127.3 (2)
H6A—C6—H6B	107.6	C3A—C11A—Se1	109.01 (17)
C8—C7—C6	114.0 (2)	C11—C11A—Se1	123.72 (17)
C8—C7—H7A	108.8		
C11A—Se1—N2—N3	-0.04 (18)	C8—C9—C10—C11	110.4 (3)

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Se1—N2—N3—C3A	0.2 (3)	C9—C10—C11—C11A	0.2 (4)
N2—N3—C3A—C11A	-0.3 (3)	N3—C3A—C11A—C11	-178.8 (2)
N2—N3—C3A—C4	178.1 (2)	C4—C3A—C11A—C11	2.9 (4)
C11A—C3A—C4—C5	108.5 (3)	N3—C3A—C11A—Se1	0.3 (3)
N3—C3A—C4—C5	-69.7 (3)	C4—C3A—C11A—Se1	-178.00 (18)
C3A—C4—C5—C6	-56.7 (3)	C10—C11—C11A—C3A	-92.0 (3)
C4—C5—C6—C7	-63.5 (3)	C10—C11—C11A—Se1	89.0 (3)
C5—C6—C7—C8	149.2 (2)	N2—Se1—C11A—C3A	-0.12 (17)
C6—C7—C8—C9	-65.1 (3)	N2—Se1—C11A—C11	179.0 (2)
C7—C8—C9—C10	-57.5 (3)		

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