

The crystal structure of a cyclodecabis[1,2,3]selenadiazole

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4,5,6,10,11,12-hexahydrocyclodeca[1,2-d:6,7-d']bis[1,2,3]selenadiazole, $C_{10}H_{12}N_4Se_2$, crystallizes in triclinic space group $P\bar{1}$ with $a = 5.4625(3)$, $b = 7.2091(4)$, $c = 8.3122(6)$ Å, $\alpha = 65.313(5)$, $\beta = 77.476(5)$, $\gamma = 77.442(5)^\circ$, $V = 287.35(4)$ Å³, $Z = 1$. The structure was refined to $R = 0.031$ and $R_w = 0.030$ for 2018 observed reflections. The molecule lies on an inversion center. The cyclodecadiene ring adopts an elongated chair conformation. The near-zero torsion angle of the elongated chair lies at the ring-fusion bonds, with a magnitude of $2.9(3)^\circ$. The five atoms of the selenadiazole ring exhibit maximum deviation $0.005(2)$ Å from planarity, with the adjacent carbon atoms lying respectively $0.020(2)$ and $0.059(2)$ Å to the same side of this plane. The torsion angles about the bonds comprising the sides of the elongated chair vary in magnitude from $61.0(2)^\circ$ to $55.7(2)^\circ$. The cyclodecadiene C=C bond lengths are $1.368(2)$ Å. The selenium-carbon bond length is $1.850(2)$ Å. The Se—N distance is quite long, $1.888(2)$ Å.

KEY WORDS: Selenadiazole, Cyclodecadiene, conformation.

Introduction

This bisselenadiazole is a precursor to 1,6-cyclodecadiyne by pyrolysis. However, yields of this pyrolysis are variable. As part of an investigation of the yield variation, we undertook to confirm in which of the two possible isomers, *syn* or *anti*, the title compound exists, by determining its crystal structure.

Experimental

The title compound was prepared according to a literature procedure.¹ Pale yellow crystals were obtained by evaporation from chloroform, m.p. $171\text{--}172^\circ$ (dec.). The data collection crystal was sealed in a capillary to prevent sublimation. The color of the crystal changed to orange, and its surfaces became crazed during data collection. Accurate unit cell parameters were obtained by least-squares refinement vs. $\sin\theta/\lambda$ values for 25 reflections ($12^\circ < \theta < 17^\circ$). Data reduction included corrections for background, Lorentz, and polarization effects. Absorption corrections were based on Ψ

scans. Standard reflections decreased by unequal amounts during data collection, and an anisotropic decay correction was applied. The structure was solved by direct methods using a partial data set which had been obtained from a fiber-mounted crystal which was lost by sublimation during data collection. Refinement was by full-matrix least squares, with neutral-atom scattering factors and anomalous dispersion corrections. All non-hydrogen atoms were refined anisotropically while all hydrogen atoms were refined isotropically.

Results and discussion

The molecule lies on a crystallographic inversion center, and thus is demonstrated to be the *anti* isomer. The molecule is illustrated in Fig. 1; the crystal data are given in Table 1; the atomic coordinates are given in Table 2, and geometric parameters are listed in Table 3. A search of the Cambridge Structural Database⁴ yields but one other crystal structure determination of a 1,2,3-selenadiazole, that of the complex⁵ of 4-methyl-1,2,3-selenadiazole with $Cr(CO)_5$. Bond distances to Se in the title structure are somewhat longer than in that Cr complex, $1.888(2)$ vs. $1.837(3)$ Å for Se—N and $1.850(2)$

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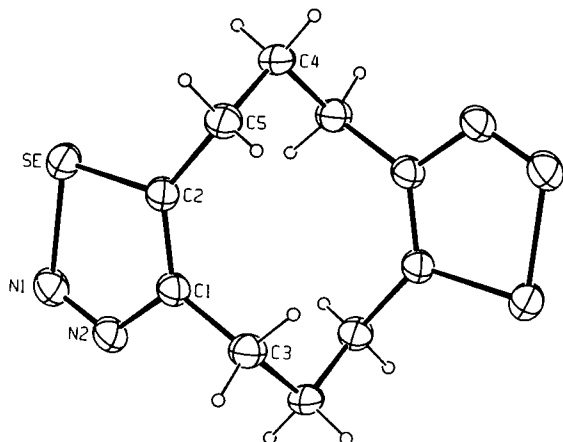


Fig. 1. Thermal ellipsoids at the 40% level and the numbering scheme for the title molecule.

Table 1. Crystal data and summary of intensity data collection and structure refinement

Compound	C ₁₀ H ₁₂ N ₄ Se ₂
Color/shape	yellow parallelepiped
Formula weight	346.2
Space group	P $\bar{1}$
Temp., °C	28
Cell constants	
<i>a</i> , Å	5.4625(3)
<i>b</i> , Å	7.2091(4)
<i>c</i> , Å	8.3122(6)
α , deg.	65.313(5)
β , deg.	77.476(5)
γ , deg.	77.442(5)
Cell volume, Å ³	287.35(4)
Formula units/unit cell	1
Dcalc, g cm ⁻³	2.000
μ_{calc} , cm ⁻¹	63.5
Diffractometer/scan	Enraf-Nonius CAD4/ ω -2 θ
Radiation, graphite monochromator	MoK α (λ = 0.71073 Å)
Max. crystal dimensions, mm	0.15 × 0.30 × 0.50
Scan width	0.60 + 0.35 tan θ
Standard reflections	300; 030; 006
Decay of standards	−15.3%
Reflections measured	2158
2 θ range, deg	2 < θ < 66
Range of <i>h</i> , <i>k</i> , <i>l</i>	+8, ±11, ±12
Reflections observed [<i>I</i> > 0]	2018
Computer programs ²	MolEN
Structure solution ³	MULTAN
No. of parameters varied	98
Weights	4F ₀ ² [$\sigma^2(I)$ + (0.02F ₀ ²) ²] ^{−1}
GOF	1.568
$R = \Sigma F_o - F_c / \Sigma F_o $	0.031
R_w	0.030
Largest feature final diff. map	0.61 e [−] Å ^{−3}

Table 2. Coordinates and equivalent isotropic thermal parameters

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²) ^a
Se	0.11869(3)	0.28516(3)	0.91783(2)	3.124(4)
N1	0.2475(3)	0.0388(2)	0.8806(2)	3.23(3)
N2	0.4496(3)	0.0578(2)	0.7729(2)	2.92(3)
C1	0.5398(3)	0.2452(2)	0.7032(2)	2.45(3)
C2	0.3975(3)	0.3925(2)	0.7612(2)	2.54(3)
C3	0.7805(3)	0.2619(3)	0.5735(2)	2.76(3)
C4	0.2407(3)	0.7687(2)	0.5940(2)	2.83(3)
C5	0.4370(3)	0.6108(2)	0.7054(2)	2.81(3)

$$^a B_{eq} = 8\pi^2/3 \sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

vs. 1.817(5) Å for Se—C, and the N1—Se—C angle is slightly larger, 86.80(7) vs. 85.3(2)°. Se—C(sp²) and particularly Se—N distances are quite variable, even within five-membered rings. The average of Se—C(sp²) distances in 32 tetraselenafulvenes⁶ is 1.893 Å, and 5-(1,2-benzoselenazol-3-yl)-3,4-dimethyl-pentadienonitrile⁷ has a Se—C distance of 1.845(11) Å. Se—N distances in 5-membered rings range from 1.777(6) and 1.792(6) Å in 2,1,3-benzoselenadiazole⁸ to 1.807(5) and 1.814(4) Å in 3,4-diphenyl-1,2,5-selenadiazole,⁹ to 1.833(7) Å in 5-(1,2-benzoselenazol-3-yl)-3,4-dimethyl-pentadienonitrile,⁷ all of which are shorter than that observed in the title compound. Dimorpholinodisilane¹⁰ has Se—N distances of 1.846(4) and 1.852(4) Å, over 0.03 Å shorter than that in the title compound.

The endocyclic torsion angles of the 10-membered ring at the ring fusion bonds are ±2.9(3)°. The 1,6-cyclodecadienyl ring adopts an elongated chair conformation^{11,12} with torsion angles: $\omega_1 = +2.9(3)^\circ$, $\omega_2 = -118.9(2)^\circ$, $\omega_3 = +61.1(2)^\circ$, $\omega_4 = +55.7(2)^\circ$ and $\omega_5 = -109.5(2)^\circ$, that are similar to the ideal long-chair conformation (of cyclodecane) having torsion angles¹² of ω_1 : C5—C2—C1—C3 = 0°; ω_2 : C2—C1—C3—C4 = −112.2°; ω_3 : C1—C3—C4—C5' = +72.7°; ω_4 : C3—C4—C5'—C2' = +72.7° and ω_5 : C4—C5'—C2'—C1' = −112.2°.

Molecular stacking is illustrated in Fig. 2. Selenadiazole rings form in-plane intermolecular contacts about inversion centers, involving the Se—N1 bond and nitrogen atom N1 at $-x, -y, 2 - z$. The Se···N1' distance is 3.094(2) Å, and the N1···N1' distance is 2.995(2) Å. The Se atom also forms a second in-plane contact with Se of another molecule at $-x, 1 - y, 2 - z$, with Se···Se distance 3.7633(3) Å. The Se—N1 bond also forms a somewhat longer, stacking contact of

Table 3. Selected bond distances, angles, and torsion angles^a (Å, °)

Se	N1		1.888(2)	C1	C3		1.501(2)	
Se	C2		1.850(2)	C2	C5		1.494(2)	
N1	N2		1.254(2)	C3	C4'		1.529(3)	
N2	C1		1.384(2)	C4	C5		1.524(2)	
C1	C2		1.368(2)					
N1	Se	C2	86.80(7)	N2	C1	C3	116.2(1)	
Se	N1	N2	110.8(1)	Se	C2	C1	108.7(1)	
N1	N2	C1	118.0(2)	Se	C2	C5	122.6(1)	
N2	C1	C2	115.7(1)					
N2	C1	C3	C4'	C2	C1	C3	C4'	-118.9(2)
Se	C2	C5	C4	C1	C2	C5	C4	109.5(2)
C1	C3	C4'	C5'	C3	C4	C5'	C2'	55.7(2)

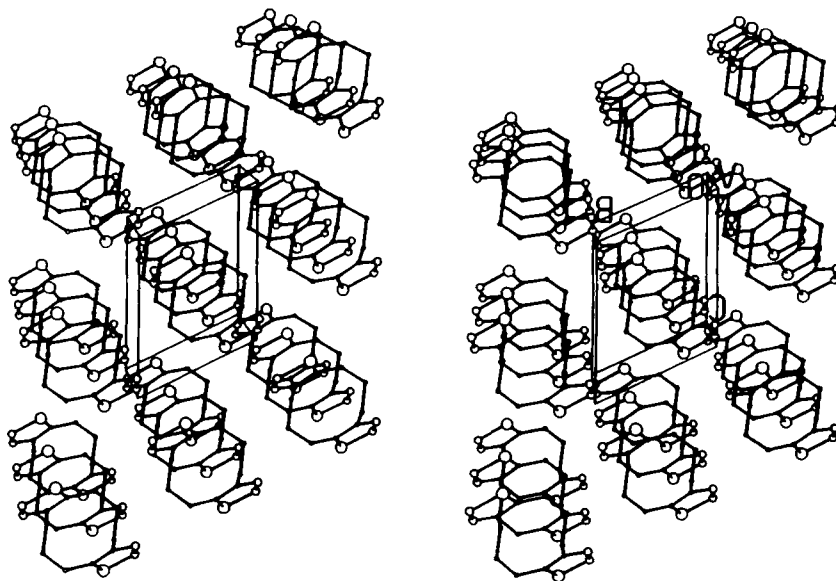
^aThe prime refers to symmetry operation $1 - x, 1 - y, 1 - z$.

Fig. 2. Stereoview of the molecular packing.

with N2 at $1 - x, -y, 2 - z$. The $\text{N1} \cdots \text{N2}$ distance is $3.377(3)$ Å, and the $\text{Se} \cdots \text{N2}$ distance is $3.614(2)$ Å.

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