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1,6-Diselenacyclodecane-3,4,8,9-tetraone Tetrakis(*O*-methyloxime)

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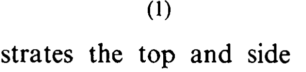
Abstract

The diselenacyclodecane ring in the title compound, $C_{12}H_{20}N_4O_4Se_2$, adopts a twist–twist–boat conformation with regular *trans* positions of the oxime groups. In this conformation, the intramolecular spatial interaction of the oxime fragments decreases to a minimum. This molecule is an *E,E,E,E* isomer with regard to the configuration of the oxime groups.

Comment

As part of our research on oxime-based macrocyclization (Shatzmiller, Menashe, Shalom & Bahar, 1991), the structure determination of 1,6-diselenacyclodecane-3,4,8,9-tetraone tetrakis(*O*-methyloxime) (1) was undertaken in order to establish the configuration of one of three products obtained from the reaction of 1,4-dibromobutan-2,3-dione bis(*O*-methyloxime) with disodium selenide.



(1)

Fig. 1 illustrates the top and side views of the conformation of (1) in its molecular crystal. In contrast to diselena[3.3]orthocyclophane, which in the solid state has a chair conformation (Okajima, Wang & Fukazawa, 1989), the diselenacyclodecane ring of (1) adopts a twist–twist–boat conformation. In this conformation, the intramolecular spatial interaction of the oxime moieties decreases to a minimum, but at the same time the possibility for conjugation in the —N=C—C=N— moiety is preserved. The C4—C3—N11—O12, C3—C4—N14—O15, C9—C8—N17—O18 and C8—C9—N20—O21 torsion angles are 179.4 (4), 180.0 (4), 180.0 (4) and −178.7 (4)°, respectively. These values, and Fig. 1, indicate that (1) is an *E,E,E,E* isomer with regard to the configuration of the oxime groups.

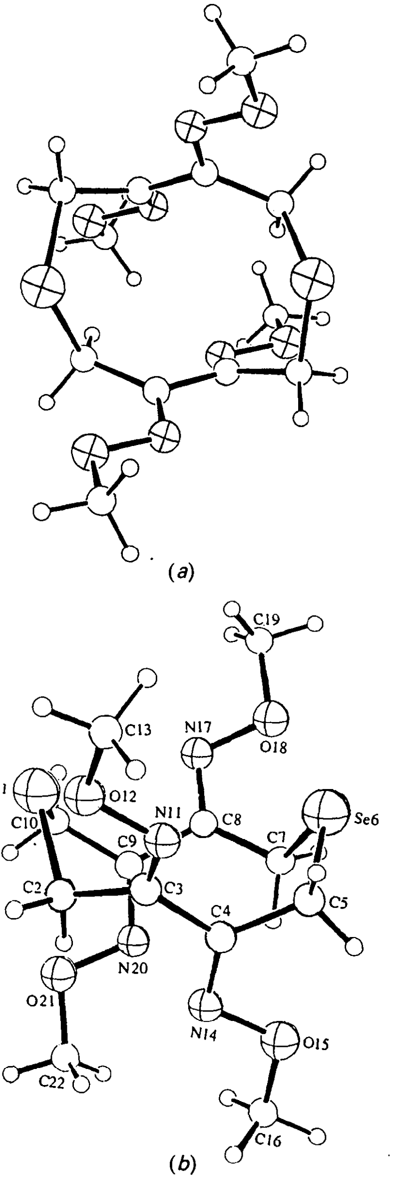


Fig. 1. Molecular conformation of the title compound: (*a*) top and (*b*) side views, showing the atom labelling. Atoms are of arbitrary size, the N, O and Se atoms being marked by crossed circles.

Experimental

Crystal data

$C_{12}H_{20}N_4O_4Se_2$
$M_r = 442.23$
Monoclinic
$P2_1/n$
$a = 8.364\ (3)$ Å
$b = 17.281\ (2)$ Å
$c = 11.940\ (1)$ Å
$\beta = 97.37\ (2)^\circ$
$V = 1711.5\ (7)$ Å^3
$Z = 4$
$D_x = 1.716$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.9-12.2^\circ$
$\mu = 4.3$ mm^{-1}
$T = 298$ K
Prism
0.30 × 0.25 × 0.20 mm
Slightly yellow

Data collection

CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical (Walker & Stuart, 1983)
$T_{\min} = 0.84$, $T_{\max} = 0.93$
3336 measured reflections
2744 independent reflections
1971 observed reflections
$[F \geq 6\sigma(F_o)]$

$R_{\rm int} = 0.028$
$\theta_{\max} = 25^\circ$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity variation: 3%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.035$
$S = 1.24$
1971 reflections
223 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max} = 0.06$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection and cell refinement: CAD-4 diffractometer software (Enraf-Nonius, 1989). Data reduction: local *CADINT* program. Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976). Geometry calculations: *PARST* (Nardelli, 1983).

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Se1	0.1341 (1)	0.3325 (1)	0.0786 (1)	0.0478 (2)
C2	0.3134 (6)	0.2708 (3)	0.1558 (4)	0.0361 (18)
C3	0.3012 (6)	0.2674 (3)	0.2791 (4)	0.0322 (17)
C4	0.4154 (7)	0.3077 (3)	0.3638 (4)	0.0342 (18)
C5	0.3608 (7)	0.3351 (3)	0.4716 (4)	0.0392 (19)
Se6	0.2360 (1)	0.4319 (1)	0.4478 (1)	0.0450 (2)
C7	0.3686 (6)	0.4933 (3)	0.3558 (4)	0.0354 (18)
C8	0.2876 (6)	0.4966 (3)	0.2365 (4)	0.0319 (18)
C9	0.3560 (7)	0.4562 (3)	0.1438 (4)	0.0311 (20)
C10	0.2440 (7)	0.4288 (3)	0.0440 (4)	0.0396 (21)
N11	0.1876 (6)	0.2314 (3)	0.3218 (3)	0.0435 (16)
O12	0.0823 (5)	0.1949 (2)	0.2364 (3)	0.0502 (16)
C13	−0.0466 (8)	0.1597 (4)	0.2857 (6)	0.0568 (26)
N14	0.5596 (6)	0.3172 (2)	0.3380 (4)	0.0396 (16)
O15	0.6560 (5)	0.3563 (2)	0.4257 (3)	0.0458 (14)
C16	0.8151 (7)	0.3678 (4)	0.3982 (6)	0.0606 (27)
N17	0.1532 (6)	0.5323 (3)	0.2052 (3)	0.0402 (16)
O18	0.0992 (5)	0.5685 (2)	0.2995 (3)	0.0461 (14)
C19	−0.0575 (7)	0.6002 (4)	0.2628 (6)	0.0519 (23)
N20	0.5092 (5)	0.4468 (2)	0.1568 (3)	0.0352 (16)
O21	0.5589 (5)	0.4094 (2)	0.0624 (3)	0.0452 (13)
C22	0.7264 (7)	0.3878 (4)	0.0867 (5)	0.0484 (25)

Table 2. *Selected geometric parameters* (Å, °)

Se1—C2	1.970 (4)	C8—N17	1.295 (6)
Se1—C10	1.970 (5)	C9—C10	1.495 (6)
C2—C3	1.490 (6)	C9—N20	1.281 (7)
C3—C4	1.474 (6)	N11—O12	1.408 (5)
C3—N11	1.294 (7)	O12—C13	1.429 (8)
C4—C5	1.497 (7)	N14—O15	1.409 (5)
C4—N14	1.293 (7)	O15—C16	1.425 (7)
C5—Se6	1.973 (5)	N17—O18	1.412 (5)
Se6—C7	1.969 (5)	O18—C19	1.436 (7)
C7—C8	1.498 (6)	N20—O21	1.408 (5)
C8—C9	1.484 (7)	O21—C22	1.443 (7)
C2—Se1—C10	102.0 (2)	C9—C8—N17	114.4 (4)
Se1—C2—C3	109.8 (3)	C8—C9—N20	116.4 (4)
C2—C3—N11	123.7 (4)	C8—C9—C10	118.8 (5)
C2—C3—C4	122.6 (4)	C10—C9—N20	124.8 (4)
C4—C3—N11	113.6 (4)	Se1—C10—C9	111.2 (3)
C3—C4—N14	116.0 (4)	C3—N11—O12	110.7 (4)
C3—C4—C5	119.8 (5)	N11—O12—C13	109.1 (4)
C5—C4—N14	124.2 (5)	C4—N14—O15	110.2 (4)
C4—C5—Se6	111.0 (3)	N14—O15—C16	111.0 (4)
C5—Se6—C7	102.2 (2)	C8—N17—O18	109.6 (4)
Se6—C7—C8	109.4 (3)	N17—O18—C19	107.4 (4)
C7—C8—N17	124.2 (4)	C9—N20—O21	110.8 (4)
C7—C8—C9	121.4 (4)	N20—O21—C22	109.7 (4)
C2—Se1—C10—C9	−45.6 (4)	Se6—C7—C8—C9	−111.0 (5)
C10—Se1—C2—C3	106.6 (4)	Se6—C7—C8—N17	67.4 (6)
Se1—C2—C3—C4	−109.9 (5)	C7—C8—N17—O18	1.5 (7)
Se1—C2—C3—N11	67.7 (6)	C7—C8—C9—C10	151.2 (5)
C2—C3—N11—O12	1.7 (7)	C7—C8—C9—N20	−28.1 (7)
C2—C3—C4—C5	150.6 (5)	C9—C8—N17—O18	180.0 (4)
C2—C3—C4—N14	−29.2 (7)	N17—C8—C9—N20	153.4 (5)
C4—C3—N11—O12	179.4 (4)	N17—C8—C9—C10	−27.3 (7)
N11—C3—C4—N14	153.0 (5)	C8—C9—C10—Se1	−78.1 (5)
N11—C3—C4—C5	−27.3 (7)	C8—C9—N20—O21	−178.7 (4)
C3—C4—N14—O15	180.0 (4)	N20—C9—C10—Se1	101.1 (5)
C3—C4—C5—Se6	−78.6 (5)	C10—C9—N20—O21	2.0 (7)
C5—C4—N14—O15	0.3 (7)	C3—N11—O12—C13	−176.6 (5)
N14—C4—C5—Se6	101.1 (5)	C4—N14—O15—C16	−179.5 (5)
C4—C5—Se6—C7	−45.3 (4)	C8—N17—O18—C19	−174.1 (5)
C5—Se6—C7—C8	106.7 (4)	C9—N20—O21—C22	−170.4 (4)

The title compound was isolated in a pure form by recrystallization of the crude mixture from methanol and was identified spectroscopically: ^{1}H NMR ($CDCl_3$): $\delta = 3.62$ (*s*, 4H, $2CH_2$) and 3.97 (*s*, 6H, $2CH_3O$). ^{13}C NMR ($CDCl_3$): $\delta = 15.6$ (*s*, CH_3), 62.4 (*s*, CH_2) and 154.6 (*s*, C=N). $\lambda_{\max}$ (pentane) = 216 ($\varepsilon = 2.18 \times 10^4$), 246 ($\varepsilon = 1.85 \times 10^4$) and 305 nm ($\varepsilon = 1.75 \times 10^3$). MS (*EI*, 7 eV): *m*/*e* 444 (^{80}Se) (M^+, 56%).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71414 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1071]

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HBF$_4$ and HBr Salts of New Chiral Cyclens

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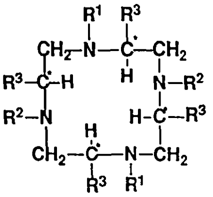
Abstract

The structures of salts of four new chiral cyclens (1,4,7,10-tetraazacyclododecane) have been determined: (2*RS*,5*RS*,8*RS*,11*SR*)-2,5,8,11-tetrabenzyl-1,4,7,10-tetraethyl-4,7,10-triaza-1-azoniacyclododecane tetrafluoroborate [$C_{44}H_{61}N_4^+.BF_4^-$, tetb = (2*RS*,5*RS*,8*RS*,11*SR*)-2,5,8,11-tetrabenzyl-1,4,7,10-tetraethylcyclen (I)], (2*R*,5*R*,8*R*,11*R*)-1,4,7,10-tetraethoxycarbonylmethyl-2,5,8,11-tetraethyl-4,10-diaza-1,7-diazoniacyclododecane bis(tetrafluoroborate) [$C_{32}H_{62}N_4O_8^{2+}.2BF_4^-$, tcte = (2*R*,5*R*,8*R*,11*R*)-1,4,7,10-tetraethoxycarbonylmethyl-2,5,8,11-tetraethylcyclen (II)], (2*R*,5*R*,8*R*,11*R*)-1,7-dibenzyl-2,5,8,11-tetraethyl-1,7-diaza-4,10-diazoniacyclododecane dibromide [$C_{30}H_{50}N_4^{2+}.2Br^-$, dbte = (2*R*,5*R*,8*R*,11*R*)-1,7-dibenzyl-2,5,8,11-tetraethyl-cyclen (III)], (2*R*,5*R*,8*R*,11*R*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,7-diaza-4,10-diazoniacyclododecane dibromide [$C_{44}H_{62}N_4^{2+}.2Br^-$, tbte = (2*R*,5*R*,8*R*,11*R*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-cyclen (IV)]. In forming salts, cyclen molecules are protonated. For the tetrafluoroborates of both (I) and (II), the 12-membered rings have a square conformation with the methylene C atoms occupying the corners. For the bromide of (III), the ring also has a square conformation with asymmetric C-atom occupied corners. The conformation of (IV)$H^{2+}.2Br^-$ differs significantly from that of the original molecule (IV). On protonation, the molecular symmetry changes from C_4 to C_2, and the corner atoms from N to asymmetric C.

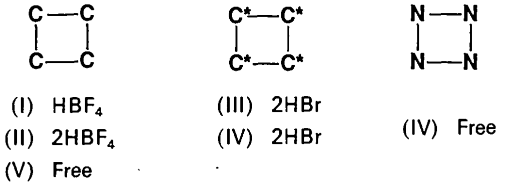
Comment

Continuing our studies on chiral cyclens and their complexes (Tsuboyama, Tsubomaya, Higashi & Yanagita, 1970; Tsuboyama *et al.*, 1981; Kobayashi, Sakurai, Hasegawa, Tsuboyama & Tsuboyama, 1982), we report the structure determinations of four new cyclen salts. The first two compounds were obtained as cyclic tetramers from the corresponding *N*-substituted chiral aziridines, (*RS*)-1-ethyl-2-benzylaziridine and (*R*)-1-ethoxycarbonylmethyl-2-ethylaziridine, in the presence of $BF_3.Et_2O$ in benzene. Compound (III), (*RRRR*)-dbte, was obtained from the tetrabenzyl cyclen (IV), (*RRRR*)-tbte (Tsuboyama *et al.*, 1970), by symmetrical debenzylation. The HBF_4 salts were crystallized from the respective reaction mixtures. The anions are trapped so tightly in the crystals that the free bases could not be obtained by washing with alkaline solution. Few crystal structure determinations of HBF_4 salts of amines have so far been reported. Both (III) and (IV) were analyzed as their hydrobromides.



(I) tetb $R^1 = R^2 =$ Et, $R^3 = CH_2Ph$
(II) tcte $R^1 = R^2 = CH_2COOEt$, $R^3 =$ Et
(III) dbte $R^1 = CH_2Ph$, $R^2 =$ H, $R^3 =$ Et
(IV) tbte $R^1 = R^2 = CH_2Ph$, $R^3 =$ Et
(V) te $R^1 = R^2 =$ H, $R^3 =$ Et

The analytical data were consistent with the presence of one BF_4^- species associated with (I), two with (II), and two Br ions with both (III) and (IV).



The symmetries of these salts were identified as C_1 for (I) and C_2 for the latter three by ^1H or ^{13}C NMR spectra. In order to confirm the above assignment, and to examine the steric effects of chirality and ring substituents on ring formation, the structure determinations were carried out by X-ray analyses.

For molecule (I), the structure of the *RRRS* molecule is shown in Fig. 1(*a*). The configurations of the four chiral centers are consistent with those assigned by the spectral data. The square conformation of the 12-membered ring is a distorted cap form, similar to that of the C_1 molecule of (*RRRS* + *SSSR*)-tbte (Sakurai, Hiramatsu, Tsuboyama & Tsuboyama, 1980). The benzyl groups attached to the asymmetric *R* and *S* C atoms point in opposite directions from the ring. The H atom at N(4) was found by