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Supramolecular structures of bis-thionooxalamic acid esters derived from (±)-cyclohexane-1,2-diamine and (±)-1,2-diphenylethylenediamine

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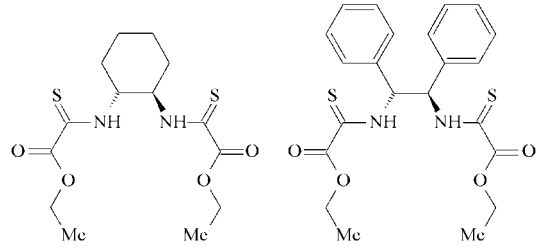
The bis-thionooxalamic acid esters *trans*-(±)-diethyl *N*,*N*′-(cyclohexane-1,2-diyl)bis(2-thiooxamate), $C_{14}H_{22}N_2O_4S_2$, and (±)-*N*,*N*′-diethyl (1,2-diphenylethane-1,2-diyl)bis(2-thiooxamate), $C_{22}H_{24}N_2O_4S_2$, both consist of conformationally flexible molecules which adopt similar conformations with approximate C_2 rotational symmetry. The thioamide and ester parts of the thiooxamate group are significantly twisted along the central C—C bond, with the S═C—C═O torsion angles in the range 30.94 (19)–44.77 (19)°. The twisted *s-cis* conformation of the thionooxamide groups facilitates assembly of molecules into a one-dimensional polymeric structure *via* intermolecular three-center C═S···NH···O═C hydrogen bonds and C—H···O interactions formed between molecules of the opposite chirality.

Comment

The self-complementary oxamic acid ester functionality is considered to be a good supramolecular building block and is expected to form an $R_2^2(10)$ hydrogen-bond motif by the interaction of two amide H atoms with two ester carbonyl groups (Blay *et al.*, 2003). However, a survey of the structures collected in the Cambridge Structural Database (Allen, 2002; Version 5.8 plus three updates) showed that during the self-assembly process, the $C(4)$ chain motif involving only the amide units competes with the cyclic $R_2^2(10)$ motif (Piotrkowska *et al.*, 2007). As the structural data of oxalamic acid esters are scarce, any generalizations about the robustness of their supramolecular synthons seem to be premature, and more information about their supramolecular structures is needed. We focused our interest on bis-thionooxamide esters expecting that, on the one hand, replacement of the amide carbonyl O atom by sulfur should enhance the acidity of the amide H atom, making it a stronger hydrogen-bond donor. On the other hand, this modification should promote hydrogen bonding to the ester carbonyl group, and thus also promote the cyclic $R_2^2(10)$ motif, because the thiocarbonyl group is a weaker hydrogen-bond acceptor than the carbonyl group. Very recently, we have reported the crystal structures of four bis-thionooxamide esters (Piotrkowska *et al.*, 2007); in the crystal structures of the homochiral compounds derived from (1*S*,2*S*)-cyclohexane-1,2-diamine, *S*-(I), and (1*R*,2*R*)-1,2-diphenylethylenediamine, *R*-(II), the molecules assemble *via* the $R_2^2(10)$ motif, forming right-handed helices and discrete dimeric assemblies, respectively.



In order to compare the self-assembly mode of enantiopure and racemic bis-thionooxamide esters, the racemic compounds *rac*-(I) and *rac*-(II) were synthesized and their crystal structures determined (Figs. 1 and 2). In the crystal structures, the symmetrical and conformationally flexible molecules are located at general positions; however, they adopt conformations that do not deviate much from C_2 symmetry. In both molecules, the torsion angles N1—C1—C2—N2, C(3,7)—N1—C1—C2 and C1—C2—N2—C(4,11), determining to a large extent the molecular conformation, have similar values (Tables 1 and 3, and Figs. 1 and 2). The latter two torsions are responsible for the orientation of the thioamide units relative to the plane of the –CH—CH– spacer. In *rac*-(II), the orientation of these groups is close to that observed in the homochiral crystal structures; the two torsion angles are 155.52 (12) and 156.60 (12)° in the racemic form, whereas in *R*-(II), they are in the range 155.8 (4)–166.4 (4)°. The difference is more pronounced in (I), where the C3—N1—C1—C2 and C1—C2—N2—C4 torsion angles are −151.70 (13) and −153.12 (13)° in *rac*-(I), whereas in homochiral *S*-(I) these angles are −94.5 (2)°, resulting in a nearly perpendicular

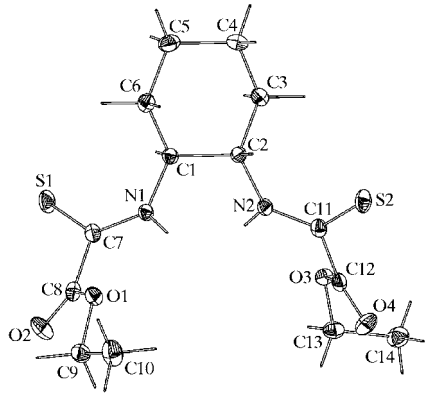


Figure 1
The molecular structure of the 1*S*,2*S* enantiomer in *rac*-(I), shown with 50% probability displacement ellipsoids.

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orientation of the thioamide group relative to the mean cyclohexane ring plane. In the racemic and enantiopure forms of (I) and (II), the thionooxamide groups are significantly twisted, with a dihedral angle between the thioamide and ester parts in the range 23.01 (6)–45.72 (6)°. Surprisingly, in the homochiral crystal structures, these groups were found in the *s-trans* conformation, whereas in the racemic forms, they are always in the *s-cis* conformation, as indicated by the values of the S═C—C═O torsion angles (Tables 1 and 3).

As mentioned earlier, in the homochiral crystal structures of (I) and (II) (Piotrkowska *et al.*, 2007), the hydrogen-bonded assemblies of molecules are formed *via* the $R_2^2(10)$ hydrogen-bond motif. However, in the crystal structures of the racemic compounds, the molecules form one-dimensional polymeric structures *via* two antiparallel *C*(5) motifs generated by N—H···O interactions between molecules of the opposite chirality (Figs. 3*a* and 4*a*). The supramolecular assemblies in the racemic crystal structures of the two studied compounds are very similar. The N—H···O hydrogen bond is part of a three-center interaction, because each thioamide H atom forms, in addition to a short contact with the carbonyl O atom, a short contact to the thiocarbonyl S atom of the same thionooxamide unit (Tables 2 and 4, and Figs. 3 and 4). The aggregate of the *S*,*S* and *R*,*R* enantiomeric molecules is further stabilized by a C—H···O interaction between the carbonyl O atom and the methine CH group of the cyclohexane ring that is located on the same side of the ring as the NH group. All of these attractive intermolecular interactions between the molecules of different chirality are optimized by a twisting of the thionooxamide groups.

To summarize, in the homo- and heterochiral crystal structures of symmetrical bis-thionooxalamic acid esters derived from *trans*-cyclohexane-1,2-diamine or 1,2-diphenylethylenediamine, the thioamide H atom is involved in

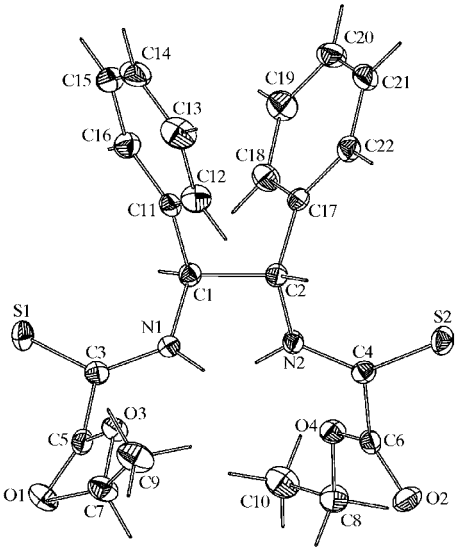

Figure 2
The molecular structure of the 1*S*,2*S* enantiomer in *rac*-(II), shown with 50% probability displacement ellipsoids.

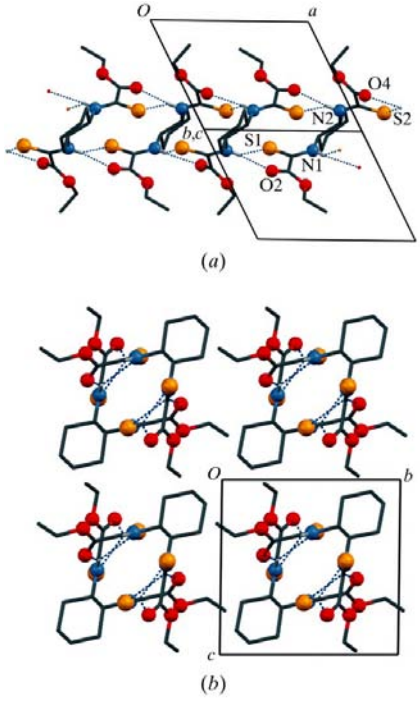

Figure 3
The crystal structure of *rac*-(I), showing (*a*) the one-dimensional aggregate of molecules formed *via* intermolecular three-center C═S···NH···O═C hydrogen bonds, and (*b*) the packing of the molecules, viewed down the *a* axis. Hydrogen bonds are represented as dashed lines and only H atoms involved in the three-center interaction are shown.

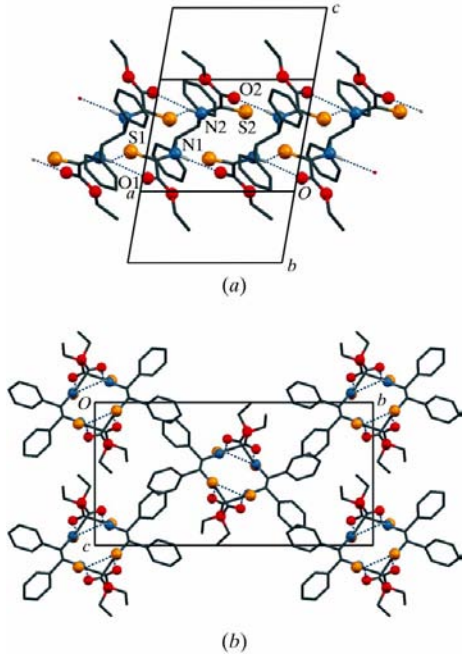

Figure 4
The crystal structure of *rac*-(II), showing (*a*) the one-dimensional polymeric structure formed *via* intermolecular three-center C═S···NH···O═C hydrogen bonds, and (*b*) the packing of the molecules, viewed down the *a* axis. Hydrogen bonds are represented as dashed lines and only H atoms involved in the three-center interaction are shown.

hydrogen bonding to the best acceptor, *viz*. the ester carbonyl O atom. In the enantiopure crystal structures, this interaction leads to the expected cyclic $R_2^2(10)$ motif, but in the case of racemic crystal structures, it generates a $C(5)$ motif, assembling molecules into an achiral one-dimensional polymeric structure.

Experimental

For the synthesis of *rac*-(I), ethyl chlorooxoacetate (2.3 ml, 20 mmol) and triethylamine (2.8 ml, 20 mmol) were added to a solution of *trans*-(±)-cyclohexane-1,2-diamine (1.14 g, 10 mmol) in chloroform (15 ml), and the mixture was kept at room temperature overnight. The reaction mixture was washed with water, dilute hydrochloric acid and saturated aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and then evaporated at reduced pressure. The resulting solid was recrystallized from chloroform–hexane to obtain 2.1 g of the product (m.p. 446–448 K). The above product (2.0 g, 6 mmol) was refluxed with Lawesson's reagent (2.86 g, 7.0 mmol) in toluene (50 ml) for 0.5 h. After removal of the solvent, the residue was purified by column chromatography on silica gel with chloroform–hexane (1:1) as an eluant to give *rac*-(I) as yellow prisms [yield 1.45 g, 70%; m.p. 384–386 K (toluene–hexane)]. ^{1}H NMR ($CDCl_3$): δ 9.18 (*s*, NH, 2H), 4.63 (*br s*, 2H), 4.35 (*m*, 4H), 2.29 (*br s*, 2H), 1.89 (*br s*, 2H), 1.45 (*d*, J = 7.8 Hz, 4H), 1.39 (*t*, J = 7.1 Hz, 6H); ν_{max} (KBr, cm^{-1}): 3292, 1702, 1269, 1246. Analysis calculated for $C_{14}H_{22}N_2O_4S_2$: C 48.54, H 6.39, N 8.09, S 18.51%; found: C 48.54, H 6.28, N 8.02, S 18.68%. For the synthesis of *rac*-(II), the oxamide (m.p. 464–466 K) prepared in an analogous way from (±)-1,2-diphenylethylenediamine (1.46 g, 3.5 mmol) was refluxed with Lawesson's reagent (1.43 g, 3.5 mmol) in toluene (50 ml) for 0.5 h. The reaction mixture was allowed to cool to room temperature and the orange precipitate was removed by filtration to give *rac*-(II) [yield 1.2 g, 77%; m.p. 431–433 K (ethanol)]. ^{1}H NMR ($CDCl_3$): δ 9.67 (*br s*, NH, 2H), 7.31–7.24 (*m*, 10H), 6.19 (*dd*, J = 5.9 and 2.9 Hz, 2H), 4.37 (*m*, 4H), 1.39 (*t*, J = 7.1 Hz, 6H); ν_{max} (KBr, cm^{-1}): 3236, 1739, 1725, 1269. Analysis calculated for $C_{22}H_{24}N_2O_4S_2$: C 59.44, H 5.44, N 6.30, S 14.43%; found: C 59.19, H 5.44, N 6.27, S 14.51%.

Compound (I)

Crystal data

$C_{14}H_{22}N_2O_4S_2$
M_r = 346.46
Triclinic, $P\overline{1}$
a = 9.6438 (10) Å
b = 9.6656 (11) Å
c = 10.3316 (11) Å
α = 85.068 (9)°
β = 63.887 (10)°
γ = 77.155 (9)°
V = 843.02 (18) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 120 (2) K
0.4 × 0.4 × 0.2 mm

Data collection

Kuma KM-4 CCD diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.840, T_{max} = 0.935
6232 measured reflections
2957 independent reflections
2587 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.072
S = 1.07
2957 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Selected torsion angles (°) for (I).

C7—N1—C1—C2	−153.12 (13)	N1—C1—C2—N2	52.61 (15)
C7—N1—C1—C6	84.98 (16)	S1—C7—C8—O2	30.94 (19)
C11—N2—C2—C1	−151.70 (13)	S2—C11—C12—O4	38.18 (19)
C11—N2—C2—C3	86.37 (15)		

Table 2
Hydrogen-bond and short-contact geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O4^{i}	0.88	2.27	3.0226 (16)	144
N1—H1N···S2^{i}	0.88	2.96	3.6806 (13)	141
N2—H2N···O2^{ii}	0.88	2.27	3.0163 (16)	143
N2—H2N···S1^{ii}	0.88	2.87	3.6093 (13)	143
C1—H1···O2^{ii}	1.00	2.64	3.3820 (18)	131
C2—H2···O4^{i}	1.00	2.52	3.2620 (18)	131

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$.

Compound (II)

Crystal data

$C_{22}H_{24}N_2O_4S_2$
M_r = 444.55
Monoclinic, $P2_1/n$
a = 9.2414 (4) Å
b = 21.7781 (10) Å
c = 11.4322 (6) Å
β = 100.273 (4)°
V = 2263.96 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 110.0 (2) K
0.30 × 0.30 × 0.08 mm

Data collection

Kuma KM-4 CCD diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.906, T_{max} = 0.979
16375 measured reflections
4613 independent reflections
3649 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.084
S = 1.08
4613 reflections
271 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 3
Selected torsion angles (°) for (II).

C3—N1—C1—C11	81.42 (15)	N1—C1—C2—N2	58.36 (14)
C3—N1—C1—C2	−155.52 (12)	S1—C3—C5—O1	44.77 (19)
C4—N2—C2—C17	81.00 (16)	S2—C4—C6—O2	43.06 (18)
C4—N2—C2—C1	−156.60 (12)		

Table 4
Hydrogen-bond and short-contact geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···O1^{i}	0.88	2.40	3.1819 (15)	147
N2—H2N···S1^{i}	0.88	2.87	3.5749 (12)	139
N1—H1N···O2^{ii}	0.88	2.15	2.9487 (15)	151
N1—H1N···S2^{ii}	0.88	3.00	3.6875 (12)	137
C1—H1···O1^{i}	1.00	2.71	3.5195 (17)	139
C2—H2···O2^{ii}	1.00	2.62	3.3781 (18)	133

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$.

All H atoms were placed at calculated positions, with C—H distances in the range 0.95–1.00 Å and N—H distances of 0.88 Å, and were refined as riding on their carrier atoms [U_{iso}(H) = 1.2U_{eq}(C,N), with the exception of methyl groups, where U_{iso}(H) = 1.5U_{eq}(C)].

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *Mercury* (Version 1.4; Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3156). Services for accessing these data are described at the back of the journal.

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