Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

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

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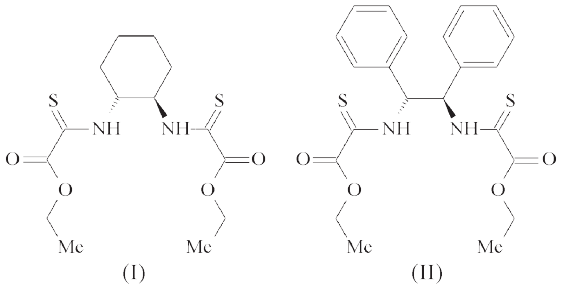
Received 8 October 2007
Accepted 10 October 2007
Online 14 November 2007

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

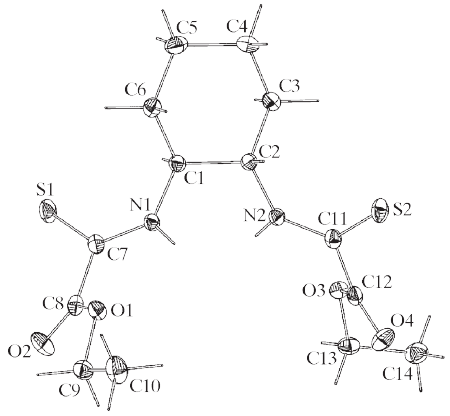


Figure 1
The molecular structure of the 1*S*,2*S* enantiomer in *rac*-(I), shown with 50% probability displacement ellipsoids.

 DOI: 10.1107/S0108270107049797