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Dimethyl *N*,*N*′-oxalamidodiethanoate

Elaine Armelin,[a] Lourdes Urpí,[a] Xavier Solans[b] and Jordi Puiggalí[a]*

[a]Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, Av. Diagonal 647, E-08028 Barcelona, Spain, and [b]Departament de Cristallografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martíi Franqués, E-08028 Barcelona, Spain
Correspondence e-mail: puiggali@eq.upc.es

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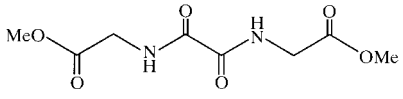
The title compound, dimethyl 2,2′-(oxalyldiimino)diethanoate, $C_8H_{12}N_2O_6$, exhibits a network of hydrogen bonds between amide and ester groups. Molecules lie on inversion centres and show a planar conformation for both the oxalamide and ester groups. The glycine residues adopt a conformation close to the polyglycine II structure.

Comment

Studies of the conformational preferences of the oxalamide group are nowadays interesting for the design of enzyme mimics and potential inhibitors (Karle *et al.*, 1994), since it corresponds to a retrobispeptide unit. In addition, molecules with oxalamide groups are capable of forming two-dimensional networks, constituting significant targets for supramolecular synthesis (Coe *et al.*, 1997). Polyoxalamides have also been widely studied in materials science because of the properties afforded by their stiff and hydrophilic units (Shalaby *et al.*, 1973; Gaymans *et al.*, 1984; Tirrell & Vogl, 1977). Our research has recently focused on the study of polyester amides derived from natural α-amino acids and various diols and dicarboxylic acids, since a biodegradable behaviour is characteristic of this kind of polymer (Paredes *et al.*, 1998). The title compound, (I), was chosen as the simplest model constituted by glycine residues in combination with oxalamide and ester groups.



(I)

The title molecule is shown in Fig. 1, with selected torsion angles and hydrogen-bond geometry in Tables 1 and 2, respectively.

The amide and ester groups are planar within experimental accuracy, with an r.m.s. distance of the atoms from the best planes passing through them of 0.0062 and 0.0075 Å for C3/N1/C4/O3/C4′/O3′/N1′/C3′ and C1/O1/C2/O2/C3, respectively.

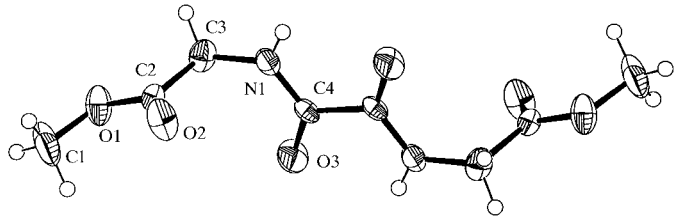


Figure 1
*ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme for non-H atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary radii.

The planar conformation of the oxalamide group is also favoured by the establishment of an intramolecular NH···OC hydrogen bond (Table 2) of a pseudo-C_5 type (a five-membered ring characteristic of amino acids, where in this case a carbonyl C atom replaces the Cα atom; Karle *et al.*, 1994). The torsion angles ψ (O1—C2—C3—N1) and φ (C2—C3—N1—C4), which define the glycine residue, are close to those found in the polyglycine II structure (−145 and 75°, respectively; Crick & Rich, 1955). However, the ψ angle deviates towards 180°, in agreement with theoretical studies (Momenteua *et al.*, 1988) on polydepsipeptide chains and also with experimental data from model compounds of polyester amides (Urpí *et al.*, 1998).

Molecules lie on inversion centres and the crystal structure is defined by a bilayered organization, as shown in Fig. 2. The packing is characterized by the establishment of a network of intermolecular hydrogen bonds that only involve the NH and CO moieties of the oxalamide and ester groups, respectively. This observation is also in agreement with theoretical investigations (Alemán *et al.*, 1995), which indicated a similar

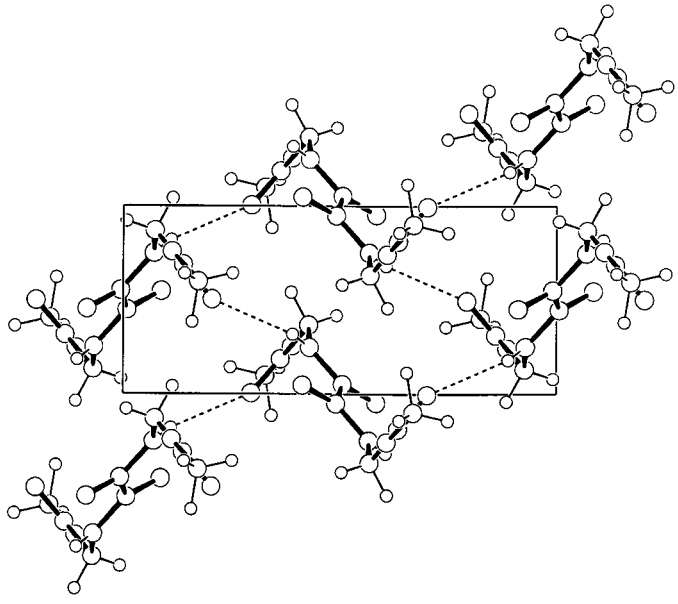


Figure 2
Packing diagram of the title compound showing the network of intermolecular hydrogen bonds between NH and CO groups (dashed lines). The view is along the crystallographic *a* axis.

strength for amide–ester and amide–amide interactions. Crystal structures of compounds with oxalamide units and neighbouring ester or acid groups show both possibilities: (*a*) 'like-to-like' amide–amide hydrogen bonds (Klaska *et al.*, 1980; Yamaguchi *et al.*, 1992; Bhattacharjee & Ammon, 1982) and (*b*) 'like-to-unlike' amide–acid (Coe *et al.*, 1997; Karle & Ranganathan, 1995) or amide–ester (Karle *et al.*, 1994) hydrogen bonds. The structure of the latter is similar to that found in the title compound. However, it should be pointed out that, in those cases, the 'like-to-unlike' interactions would be favoured by the steric hindrance of lateral groups (compounds with aminoisobutyryl or leucyl residues) or the capability to form additional hydrogen bonds between the oxalamide carbonyl and the hydroxyl of the acid groups.

Two C—H···O interactions found in the crystal may also be classified as hydrogen bonds (Table 2). One of these interactions involves the ester group, whereas the second one affects the oxalamide unit.

Experimental

A solution of glycine methyl ester hydrochloride (0.2 mol) and triethylamine (0.4 mol) in chloroform (250 ml) was treated with a solution of oxaloyl chloride (0.1 mol) in chloroform (150 ml), which was added slowly while maintaining the temperature at 273 K. After 1.5 h at room temperature, the solution was evaporated, yielding a white powder which was recrystallized from 2-propanol (yield 47%, m.p. 434 K). Colourless prismatic crystals were obtained by vapour diffusion (293 K) of a 46:54 (*v*/*v*) chloroform/carbon tetrachloride mixture, as precipitant, into a 56:44 (*v*/*v*) chloroform/carbon tetrachloride solution (concentration 2.6 mg ml^{-1}).

Crystal data

$C_8H_{12}N_2O_6$
M_r = 232.20
Monoclinic, $P2_1/n$
a = 10.4122 (11) Å
b = 4.7567 (8) Å
c = 11.6778 (16) Å
β = 108.168 (10)°
V = 549.54 (13) Å^3
Z = 2
D_x = 1.403 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.0–28.5°
μ = 1.05 mm^{-1}
T = 293 (2) K
Prism, colourless
0.24 × 0.14 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
999 measured reflections
999 independent reflections
880 reflections with $I > 2\sigma(I)$
θ_{max} = 67.9°
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 5$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.155
S = 1.10
999 reflections
83 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1062P)^2 + 0.1100P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.015
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected bond angles (°).

C1—O1—C2—C3	−178.58 (17)	C4—N1—C3—C2	80.54 (19)
C4^i—C4—N1—C3	−179.01 (14)	O1—C2—C3—N1	−162.85 (14)

Symmetry code: (i) $2-x, -y, 1-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O2^i	0.77 (2)	2.26 (2)	2.886 (2)	139 (2)
N1—H1N···O3^{ii}	0.77 (2)	2.37 (2)	2.707 (2)	108 (2)

Symmetry codes: (i) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $2-x, -y, 1-z$.

H atoms were found in difference Fourier maps. However, those not linked to the amide N atoms were refined using constraints (C—H = 0.96–0.97 Å).

Data collection: *CAD*-4 *Software* (Kiers, 1994); cell refinement: *SETANG* and *LS* in *CAD*-4 *Software*; data reduction: local program; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1454). Services for accessing these data are described at the back of the journal.

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