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Intermolecular contacts in the crystal packing of 2,2′-(*N*,*N*′-oxalyldiimino)-bis(3-phenylpropanamide) dimethyl sulfoxide solvate

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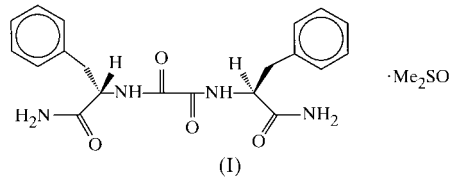
In the title compound, $C_{20}H_{22}N_4O_4\cdot C_2H_6OS$, two distinct hydrogen-bond systems connect oxalamide groups in one pattern and primary amide groups in the other to form a two-dimensional network perpendicular to the *c* axis. These hydrophilic layers are joined to the three-dimensional structure through C—H$\cdots\pi$ interactions. The hydrogen-bonded waved layers shape holes which are occupied by disordered dimethyl sulfoxide solvent molecules.

Comment

In recent years, there has been increased interest in the investigation of retro-bipeptides with an oxalamide unit (–NH—CO—CO—NH–) for two reasons: (i) to modify peptides in order to gain peptidomimetics useful for medical treatment (Karle *et al.*, 1994; Karle & Ranganathan, 1995) and (ii) to model synthons which generate supramolecular aggregates (Coe *et al.*, 1997; Nguyen *et al.*, 1998). Our interest has focused on the retro-bipeptides, which serve as gelators of many organic solvents and water (Jokić *et al.*, 1995; Makarević *et al.*, 2001). The gelling properties of these compounds depend on the stereochemistry of amino acids substituted at the ends of the oxalamide units. Generally, it appears that retro-bipeptide-containing amino acids of the same chirality are good gelators, whereas *meso* forms or racemates are found to be poor gelators or are not gelators at all. Therefore, detailed analysis of hydrogen-bond systems in crystal structures of these retro-bipeptides and other molecules closely related to them is required. This analysis points out the interactions responsible for the aggregation-forming holes, which can serve as solvent traps during gel formation.

In this paper, the molecular structure of the title compound, (I), is presented. The *ORTEP*II (Johnson, 1976) plot (Fig. 1) shows that the primary amide groups, as well as the phenylalanine side chains, are oriented on the same side of the central oxalamide unit. The pairs of torsion angles (φ,ψ) and (φ',ψ') are close to those found in the parallel β-sheets in peptides (Table 1). Torsion angles ω, ω', φ, φ', ψ, ψ', χ and χ' are labelled according to the literature (Karle *et al.*, 1994). The large difference in the χ and χ' angles (Table 1) reveals perpendicular and parallel orientations of amino acid moieties toward the central oxalamide unit, respectively (Fig. 1).



(I)

Crystal packing is realised by hydrogen bonds connecting: (i) oxalamide$\cdots$oxalamide units and (ii) terminal amide$\cdots$terminal amide groups (Table 2, Figs. 2*a* and 2*b*, respectively). The former hydrogen bonds form a fourth level pattern with the graph-set descriptor $R_2^2(4)$ (Bernstein *et al.*, 1995) connecting molecules translated along the *a* axis (Fig. 2*a*). These interactions include two intramolecular hydrogen bonds, N1—H1—O11 and N11—H11$\cdots$O1, and two intermolecular hydrogen bonds, N1—H1$\cdots$O1^{i} and N11—H11$\cdots$O11^{ii} (Table 2; symmetry codes: (i) $1+x, y, z$; (ii) $x-1, y, z$). The pattern formed is also stabilized by $\pi\cdots\pi$ interactions between the phenyl rings. The latter hydrogen-bond pattern involves terminal primary amide groups with both of their H atoms *syn* and *anti*. The *anti*-H atoms of both terminal amide groups act as proton donors to O atoms of amide groups of the molecules translated along **a** (N3—H32$\cdots$O2^{ii} and N31—H312$\cdots$O21^{i}, Table 2). The *syn*-H atoms participate in hydrogen bonds with O atoms of primary amide groups operated by symmetry 2_1 along **b** (N3—H31$\cdots$O21^{iii} and N31—H311$\cdots$O2^{iv}, Table 2; symmetry codes: (iii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$). The pattern described here is different to the one discussed by Chang *et al.* (1993), which is the most common hydrogen-bonding pattern formed by primary amides (Leiserowitz & Schmidt, 1969). However, fragmental similarity can be seen in the crystal structure of adipamide (Hospital & Housty, 1966) with primary amide groups hydrogen bonded along the twofold screw axis. On the

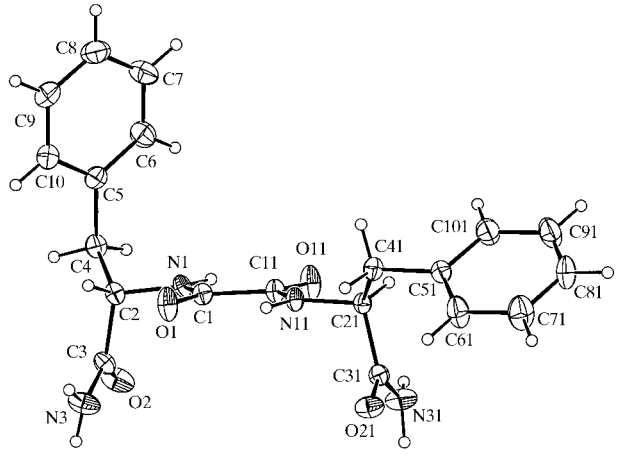


Figure 1
The molecular structure of (I) showing 30% probability displacement ellipsoids.

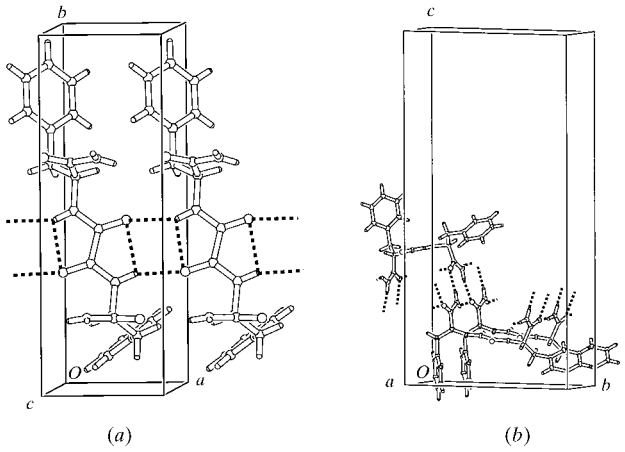


Figure 2
Hydrogen-bonding patterns formed by (*a*) oxalamide groups and (*b*) primary amide groups.

contrary, in the title molecule, the hydrogen-bonded pattern is perpendicular to the twofold screw axis along **b**. The rest of the adipamide molecule develops a centrosymmetric arrangement. In the crystal of the title molecule, the wave-shaped pattern of the two-dimensional hydrogen-bond system forms holes occupied by disordered dimethyl sulfoxide molecules (Fig. 3). Such packing also places phenyl rings of neighbouring molecules in a perpendicular orientation enabling C—H$\cdots\pi$ interactions. One of these interactions, C81—H81$\cdots$Ph(1) (H$\cdots$centroid 3.286 Å) connects molecules along **b** whereas C7—H7$\cdots$Ph(1) (H$\cdots$centroid 3.076 Å) and C101—H101$\cdots$Ph(2) (H$\cdots$centroid 3.116 Å) connect layers along **c** (Fig. 3). Thus, C—H$\cdots\pi$ interactions complete the three-dimensional network.

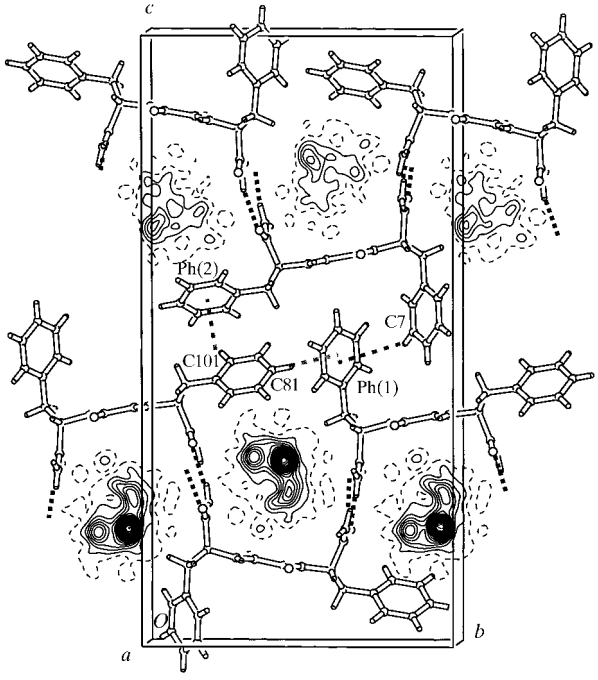


Figure 3
The crystal packing of (I). Black dashed lines are hydrogen bonds and gray dashed lines mark the C—H$\cdots\pi$ T-shape interactions. Electron density of dimethyl sulfoxide in voids, calculated by the *SQUEEZE* procedure (Spek, 1999), is also shown.

Experimental

Details of the synthesis of the title compound, (I), will be described elsewhere (Makarević *et al.*, 2001).

Crystal data

$C_{20}H_{22}N_4O_4\cdot C_2H_6OS$
M_r = 460.54
Orthorhombic, $P2_12_12_1$
a = 5.1830 (5) Å
b = 15.220 (3) Å
c = 29.630 (10) Å
V = 2337.4 (9) Å^3
Z = 4
D_x = 1.309 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 21 reflections
θ = 9.1–18.9°
μ = 1.57 mm^{-1}
T = 295 (3) K
Needle, colourless
0.32 × 0.14 × 0.04 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (*PLATON*; Spek, 1999)
T_{min} = 0.744, T_{max} = 0.943
2786 measured reflections
2786 independent reflections
1888 reflections with $I > 2\sigma(I)$
θ_{max} = 74.2°
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 36$
3 standard reflections
frequency: 180 min
intensity decay: 1%

Refinement

Refinement on F^2
$R(F)$ = 0.043
$wR(F^2)$ = 0.120
S = 1.01
2786 reflections
277 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

The structure contains disordered molecules of dimethyl sulfoxide. The electron density of dimethyl sulfoxide was taken into account with the *SQUEEZE* procedure in *PLATON* (Spek, 1999), based on iterative difference Fourier syntheses (van der Sluis & Spek, 1990). After two cycles of the *SQUEEZE* procedure and least-squares

Table 1
Selected torsion angles (°).

C11—C1—N1—C2 (ω)	174.50 (13)	C1—C11—N11—C21 (ω')	174.95 (10)
C1—N1—C2—C3 (φ)	−92.83 (18)	C11—N11—C21—C31 (φ')	−95.3 (2)
N1—C2—C3—N3 (ψ)	94.1 (3)	N11—C21—C31—N31 (ψ')	91.0 (3)
N1—C2—C4—C5 (χ)	−68.5 (3)	N11—C21—C41—C51 (χ')	178.46 (16)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1^{i}	0.89 (4)	2.14 (4)	2.994 (3)	159 (4)
N1—H1$\cdots$O11	0.89 (4)	2.35 (5)	2.712 (3)	104 (3)
N11—H11$\cdots$O1	0.85 (3)	2.30 (3)	2.695 (3)	109 (2)
N11—H11$\cdots$O11^{ii}	0.85 (3)	2.20 (3)	2.985 (3)	154 (3)
N3—H31$\cdots$O21^{iii}	0.85 (4)	2.18 (3)	2.988 (3)	159 (3)
N3—H32$\cdots$O2^{ii}	0.87 (5)	2.19 (5)	2.945 (4)	145 (4)
N31—H311$\cdots$O2^{iv}	0.90 (3)	2.04 (3)	2.909 (3)	163 (3)
N31—H312$\cdots$O21^{i}	0.80 (4)	2.23 (4)	2.954 (4)	151 (3)

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

refinement, convergence was reached. The total number of electrons in the solvent region (576 Å^3 in one unit cell) is 173 electrons, calculated by *SQUEEZE* on data corrected for the absorption. This number of electrons is in agreement with the result of thermogravimetric analysis. The experimental weight loss by heating the sample from 323 to 510 K was 16.4%. It corresponds to one molecule of dimethyl sulfoxide per formula unit. Thus, one molecule of dimethyl sulfoxide was added to the chemical formula, chemical formula weight, crystal density and linear absorption coefficient (μ). The contribution of dimethyl sulfoxide to the observed structure factors was removed by the *SQUEEZE* procedure and final refinement cycles were performed without atoms of dimethyl sulfoxide. The H atoms were calculated at ideal positions and constrained to ride on atoms to which they are bonded. Exceptions are H atoms involved in hydrogen bonds which were refined without restraints. Final F_o/F_c tables were calculated with the program *PLATON* (Spek, 1999) and include the solvent contribution.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) and *PLATON* (Spek, 1999); molecular graphics: *PLATON*; software used to prepare material for publication: *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1478). Services for accessing these data are described at the back of the journal.

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