

## *N,N'*-Bis(methoxycarbonylmethyl)- terephthalamide

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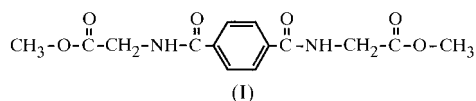
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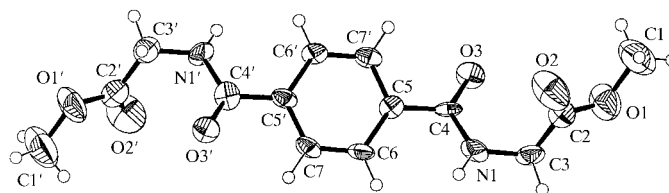
Molecules of the title compound, dimethyl *N,N'*-(1,4-benzenedicarboxamido)diacetate,  $C_{14}H_{16}N_2O_6$ , lie on inversion centres and are hydrogen bonded along a single direction that runs parallel to the crystallographic *b* axis. Glycine residues adopt a conformation which deviates slightly from that characteristic of the polyglycine II structure. An angle close to  $27^\circ$  is found between the planar amide groups and the plane of the aromatic ring.

### Comment

Poly(ester amide)s derived from natural amino acids have recently been suggested as a potential family of biodegradable polymers (Paredes, Rodríguez-Galán & Puiggali, 1998; Paredes, Rodríguez-Galán, Puiggali & Péraire, 1998). In order to obtain data for the determination of these polymer structures, different model compounds have been solved (Urpí *et al.*, 1998*a,b*, 1999). The title compound, (I), has been chosen for the study of polymers derived from terephthalic acid, glycine and different diols, since it may be a model for the common sequence  $-\text{OCOCH}_2\text{NHCOC}_6\text{H}_4\text{CONHCH}_2\text{COO}-$ . The model molecule is shown in Fig. 1, and selected rotation angles and hydrogen-bond geometry are reported in Tables 1 and 2, respectively.



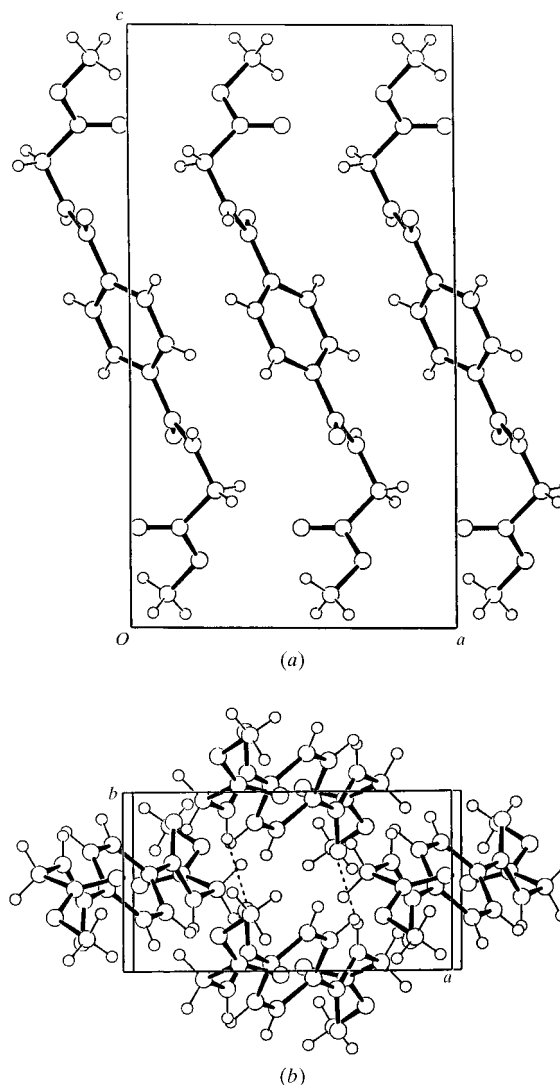
The amide and ester groups and the benzene ring are planar within experimental accuracy, with root-mean-square distances of the atoms from the best planes defined by them of 0.011, 0.034 and 0.014 Å for C3/N1/C4/O3/C5, C1/O1/C2/O2/C3 and C4/C5/C6/C7/C7'/C6'/C5'/C4', respectively. The molecule is centrosymmetric and consequently the torsion angles of its two halves are equal but with opposite signs. The glycine residues are characterized by the torsion angles  $\varphi$  (C2—C3—N1—C4) and  $\psi$  (O1—C2—C3—N1), the values of which are very close to those found in the polyglycine II



**Figure 1**

A view of (I) with the atom-numbering scheme for the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as circles with arbitrary radii.

structure ( $75$  and  $-145^\circ$ , respectively; Crick & Rich, 1955). The molecular conformation is also characterized by the N1—C4—C5—C6 torsion angle of  $156.09(13)^\circ$ , which clearly deviates from  $180^\circ$ . Thus, a displacement of the planar amide group out of the plane of the benzene ring ( $27^\circ$ ) is produced. This departure from a planar structure (favoured by resonance



**Figure 2**

The crystal packing of (I) shown with views normal to (a) the *ac* and (b) the *bc* plane. Hydrogen bonds are established along a single direction that runs practically parallel to the *a* axis.

energy of the conjugate system) can be explained by taking into account a combination of two factors: (i) steric hindrances between the H and O atoms of the amide groups and the nearest H atoms of the aromatic ring; (ii) the establishment in the crystal of intermolecular hydrogen bonds between the amide groups of adjacent molecules. Similar values in the 20–30° interval for the internal rotation angle have been found for different model compounds of aromatic polyamides (Blake & Small, 1972; Palmer & Brisse, 1980; Harkema & Gaymans, 1977) and poly(ester amide)s (Cesari *et al.*, 1976). The molecular packing (Fig. 2) is characterized by the establishment of hydrogen bonds along a single direction. A standard geometry is found between the hydrogen-bonded molecules, which are not shifted along the molecular axis direction. A twofold screw axis parallel to the *b* axis relates the non-hydrogen-bonded molecules of the unit cell. The aromatic rings of these two molecules adopt a disposition close to perpendicular, with a distance of 5.13 Å between the centers of the two rings. This geometry is in agreement with recent calculations on benzene dimers (Chipot *et al.*, 1996) that show the T-shaped disposition to be more stable than the stacked one. In the same sense, a T-shaped disposition of aromatic rings seems to be preferred in proteins (Hunter *et al.*, 1991).

## Experimental

The title compound was synthesized by the reaction of a solution of glycine methyl ester hydrochloride (0.02 mol) and triethylamine (0.04 mol) in chloroform (30 ml) with a solution of terephthaloyl chloride (0.01 mol) in chloroform (20 ml), which was added slowly while maintaining the temperature at 273 K. After 2 h at room temperature, the solution was evaporated yielding a yellow powder that was recrystallized from water (yield 75%, m.p. 435 K). Colorless prismatic crystals were obtained by vapor diffusion (293 K) of a 91:9 (*v/v*) water/2-propanol solution (concentration 3.6 mg ml<sup>-1</sup>) against 100% water used as precipitant.

### Crystal data

C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>  
*M<sub>r</sub>* = 308.29  
 Monoclinic, *P*2<sub>1</sub>/*a*  
*a* = 8.9889 (10) Å  
*b* = 4.977 (2) Å  
*c* = 16.790 (4) Å  
 $\beta$  = 90.900 (10)°  
*V* = 751.1 (4) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.363 Mg m<sup>-3</sup>  
 Cu *K*α radiation  
 Cell parameters from 20 reflections  
 $\theta$  = 8–35°  
 $\mu$  = 0.916 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, colourless  
 0.20 × 0.10 × 0.05 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$  scans  
 2237 measured reflections  
 1172 independent reflections  
 1029 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.031

$\theta_{\max}$  = 65.77°  
*h* = -10 → 10  
*k* = 0 → 5  
*l* = -19 → 19  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 0.5%

**Table 1**

Selected torsion angles (°).

N1–C4–C5–C6	156.09 (13)	N1–C3–C2–O1	-152.04 (17)
C4–N1–C3–C2	65.2 (2)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1...O3 <sup>i</sup>	0.86	2.08	2.868 (2)	152

Symmetry codes: (i) *x*, 1 + *y*, *z*.

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.069$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$wR(F^2) = 0.175$	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 1.491	( $\Delta/\sigma$ ) <sub>max</sub> < 0.001
1172 reflections	$\Delta\rho_{\max} = 0.31 \text{ e \AA}^{-3}$
102 parameters	$\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$

H atoms were placed in calculated positions and refined riding on the atom to which they are attached (N–H = 0.86 Å and C–H = 0.93–0.97 Å), with a fixed isotropic displacement parameter.

Data collection: *CAD-4 Software* (Kiers, 1994); cell refinement: *CAD-4 Software*; data reduction: local program; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1152). Services for accessing these data are described at the back of the journal.

## References

- Blake, C. C. F. & Small, R. W. H. (1972). *Acta Cryst.* **B28**, 2201–2206.  
 Cesari, M., Perego, G. & Melis, A. (1976). *Eur. Polym. J.* **12**, 585–590.  
 Chipot, C., Jaffe, R., Maigret, B., Pearlman, D. A. & Kollman, P. A. (1996). *J. Am. Chem. Soc.* **118**, 11217–11224.  
 Crick, F. H. C. & Rich, A. (1955). *Nature (London)*, **176**, 780–781.  
 Harkema, S. & Gaymans, R. J. (1977). *Acta Cryst.* **B33**, 3609–3611.  
 Hunter, C. A., Singh, J., Thornton, J. M. (1991). *J. Mol. Biol.* **218**, 837–850.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Kiers, C. (1994). *CAD-4 Software*. UNIX Version. Enraf–Nonius, Delft, The Netherlands.  
 Palmer, A. & Brisse, F. (1980). *Acta Cryst.* **B36**, 1447–1452.  
 Paredes, N., Rodríguez-Galán, A. & Puiggali, J. (1998). *J. Polym. Sci. Polym. Chem. Ed.* **36**, 1271–1282.  
 Paredes, N., Rodríguez-Galán, A., Puiggali, J. & Peraire, C. (1998). *J. Appl. Polym. Sci.* **69**, 1537–1549.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
 Urpí, L., Rodríguez-Galán, A. & Puiggali, J. (1998a). *Macromol. Chem. Phys.* **199**, 1167–1173.  
 Urpí, L., Rodríguez-Galán, A. & Puiggali, J. (1998b). *J. Chem. Crystallogr.* **28**, 605–610.  
 Urpí, L., Rodríguez-Galán, A. & Puiggali, J. (1999). *J. Chem. Crystallogr.* **29**, 1055–1059.