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A model compound for poly(ester amide)s: diethyl-3,9-diaza-4,8-dioxoundecanedioate

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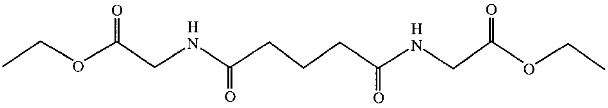
The compound diethyl-3,9-diaza-4,8-dioxoundecanedioate (EtGGGEt) has crystallized in the space group $P2_1$ with cell parameters a = 8.267(2), b = 4.853(4), c = 20.361(6) Å, β = 97.96(2)°. The crystal structure has been solved by direct methods and refined using the full matrix least squares methodology. There is one molecule in the asymmetric unit, in spite of its symmetric constitution. The central part of the molecule, the glutaramide moiety, has a partial folded conformation ($\mathrm{T\bar{S}TTST}$), which differs from the all *trans* conformation found in related moieties but with an even number of carbon atoms. The two flanking glycine residues have a different conformation one from each other; the first one adopts the standard conformation ($\psi = -156.5°$, $\varphi = 73°$), while the second one has an unusual conformation. In this glycine the oxygen atom has a big temperature factor and it is disordered in two positions. Both facts, conformation and disorder of the second glycine, seem to be due to improvement of contacts with neighboring molecules. The molecules are hydrogen bonded along the b axis, forming infinite rows with the same sense of orientation, so the crystal has a polar structure.

KEY WORDS: Poly(ester amide)s; glycine; glutaric acid; model compound; nylons; X-ray diffraction.

Introduction

There has been an increasing interest in the study of poly(ester amide)s due to their potential biodegradability and adequate mechanical properties.[1] In particular, those polymers derived from natural amino acids appear to have an enhanced susceptibility to degradation. As part of our work on the structural study of new poly(ester amide)s,[2–4] we report here the structure of the model compound diethyl-3,9-diaza-4,8-dioxoundecanedioate (EtGGGEt), (see Scheme 1).



Scheme 1

Experimental

Synthesis

For the preparation of the title compound, 3.6 mmol of glutaryl dichloride were poured into a chloroform solution of 7.2 mmol of glycine ethyl ester hydrochloride and 14.4 mmol of triethylamine. After two hours of stirring, the solution was evaporated to dryness. The solution was extracted with ethyl acetate and the product was recovered by evaporation of solvent. For purification, it was twice recrystallized from toluene (m.p. 364-365 K, yield 80%).

X-ray diffraction

Crystals were obtained by vapor diffusion from a dibutylether–acetonitrile (7:3, relation in volume) solution (concentration 3.33 mg/ml) equilibrated

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Table 1. Crystal Data and Structure Refinement

Compound	$CH_3CH_2OC(O)CH_2NHC(O){-}(CH_2)_3{-}$ $C(O)NHCH_2C(O)OCH_2CH_3$
CCDC deposit no.	CCDC-1003/5668
Color/shape	Colorless/needle
Chemical formula	$C_{13}H_{22}N_2O_6$
Formula weight	302.33
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a = 8.267(2) Å	
b = 4.853(4) Å β = 97.96(2)°	
c = 20.861(6) Å	
Volume, Å^3	809.0(7)
Z	2
Density (calculated), mg/m^3	1.241
Absorption coefficient, mm^{-1}	0.829
Diffractometer/scan	CAD4-Enraf Nonius/ω-θ
θ range for data collection, deg	2.19–56.96
Reflections measured	2526
Independent/observed reflections	1245 (Rint = 0.0475)/1245 [$F > 2\sigma(F)$]
Data/restraints/parameters	1245/9/202
Goodness of fit on F^2	1.160
Final R indices [$F > 4\sigma(F)$]	$R1$ = 0.0665, $wR2$ = 0.1566
R indices (all data)	$R1$ = 0.1186, $wR2$ = 0.1967

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameter (Å^2) of Non-Hydrogen Atoms for EtGGGEt

	x	y	z	U_{eq}
C1	0.704(1)	0.663(3)	0.0055(4)	0.113(4)
C2	0.835(1)	0.483(2)	0.0382(4)	0.103(3)
O3	0.7843(6)	0.365(1)	0.0961(2)	0.083(2)
C4	0.894(1)	0.206(2)	0.1322(4)	0.073(2)
O4	1.0286(8)	0.170(2)	0.1206(3)	0.112(3)
C5	0.8230(9)	0.080(2)	0.1894(4)	0.075(2)
N6	0.9428(8)	0.002(1)	0.2435(3)	0.072(2)
C7	1.022(1)	0.188(2)	0.2836(4)	0.067(2)
O7	0.9953(9)	0.433(1)	0.2730(3)	0.101(2)
C8	1.143(1)	0.087(2)	0.3381(3)	0.078(2)
C9	1.140(1)	0.229(2)	0.4040(4)	0.084(2)
C′8	1.270(1)	0.126(2)	0.4562(3)	0.083(2)
C′7	1.274(1)	0.258(2)	0.5220(4)	0.075(2)
O′7	1.260(1)	0.507(1)	0.5294(3)	0.121(3)
N′6	1.2888(9)	0.093(1)	0.5745(3)	0.082(2)
C′5	1.304(1)	0.191(2)	0.6409(4)	0.101(3)
C′4	1.440(1)	0.074(2)	0.6840(5)	0.089(3)
O′4A	1.557(3)	0.02(1)	0.654(1)	0.14(2)
O′4B	1.480(3)	−0.172(4)	0.679(1)	0.126(9)
O′3	1.4668(8)	0.178(2)	0.7433(3)	0.104(2)
C′2	1.604(1)	0.067(3)	0.7872(5)	0.144(6)
C′1	1.628(2)	0.215(4)	0.8493(5)	0.161(6)

Table 3. Selected Geometric Parameters [Å, °] for EtGGGEt

(a) Selected torsional angles			
Cl—C2—O3—C4	−177.3(8)		
C2—O3—C4—C5	−176.6(8)		
O3—C4—C5—N6	−156.5(7)		
C4—C5—N6—C7	73(1)		
C5—N6—C7—C8	179.8(7)		
N6—C7—C8—C9	−137.3(8)		
C7—C8—C9—C′8	−177.2(7)		
C8—C9—C′8—C′7	179.9(8)		
C9—C′8—C′7—N′6	134.0(9)		
C′8—C′7—N′6—C′5	175.8(8)		
C′7—N′6—C′5—C′4	−129(1)		
N′6—C′5—C′4—O′3	174(1)		
C′5—C′4—O′3—C′2	−179(1)		
C′4—O′3—C′2—C′1	176(1)		
(b) Hydrogen-bonding geometry			
D—H···A	D---H	H···A	D---H···A
N6—H6···O7$_{(i)}$	2.847(9)	1.991(9)	173.8(3)
N′6—H′6···O′7$_{(i)}$	2.98(1)	2.14(1)	166.3(3)
(c) Contact distances			
O′4A···C8$_{(ii)}$	3.25(3)		
O′4A···C9$_{(ii)}$	3.25(2)		
O′4A···C′8$_{(ii)}$	3.42(2)		
O′4B···C8$_{(ii)}$	3.38(2)		
O′4B···C′5$_{(i)}$	3.45(3)		
O′7···C′8$_{(iii)}$	3.36(1)		

Symmetry codes:
(i) x, y − 1, *z*; *(ii)* 1 − *x*, −0.5 + *y*, 1 − *z*; *(iii) x*, 1 + *y*, *z*.

against a reservoir with dibutylether–acetonitrile (9:1, relation in volume).

The main characteristics of data collection are indicated in Table 1. The software used for cell refinement and for data collection was the software of CAD4 in UNIX version.[5] Data reduction was carried out with a local program.

The solution of the structure has been obtained by direct methods, with a standard run of the program SHELXS-86.[6] The refinement was carried out with the program SHELXL-93[7] and the main parameters about refinement are summarized in Table 1. After doing 10 cycles of isotropic refinement and 30 cycles of anisotropic refinement of all non-hydrogen atoms, the hydrogen atoms were placed at calculated positions. Some of the H atoms were possible to be located in the difference Fourier map, but not all. We decided to place all H atoms at calculated positions to increase the reflections/parameters ratio. All H atoms were thus located at ideal positions and were refined riding on their bonded atoms with a fixed isotropic displacement parameter 1.5 (for methyl H atoms) or 1.2 (for all other H atoms) times the value of the equivalent isotropic displacement parameter of the atom to which they were attached.

A bond length restraint was necessary to be applied to the terminal ethyl bonds. The O′4 atom is disordered in two positions (61% in the main position (B) and 39% in the secondary position (A)). This atom has a big temperature factor, so it has been refined with a rigid bond restraint for the components of the anisotropic displacement parameters of the two positions.

The relatively high *R* value and the not very high resolution are related to the small dimensions of the crystal. The drawings were made with molecular graphics programs ORTEP-II[8] and CERIUS 3.1.[9]

Discussion

The values of bond distances and bond angles found in the studied compound agree with current values found in the literature for methylene, esther, and amide groups. The conformation of the central part of the molecule, the glutaramide moiety, is $T\bar{S}TTST$ (Table 3a). This result differs from the all *trans* conformation expected for even-even nylons[10] and also found in the even suberamide unit of the related model compound diethyl-3,12-diaza-4,11-dioxotetradecanedioate (EtGSGEt).[4] However, the skew torsion angles are in full agreement with the γ conformation characteristic of nylons derived from odd diacids.[10]

In spite of its chemical symmetry, the molecule is asymmetric and so the conformation of the two glycine residues is different (Fig. 2 and Table 3a). Whereas, the torsion angles ψ (O—CO—CH$_2$—NH) and φ (CO—CH$_2$—NH—CO) of one residue are

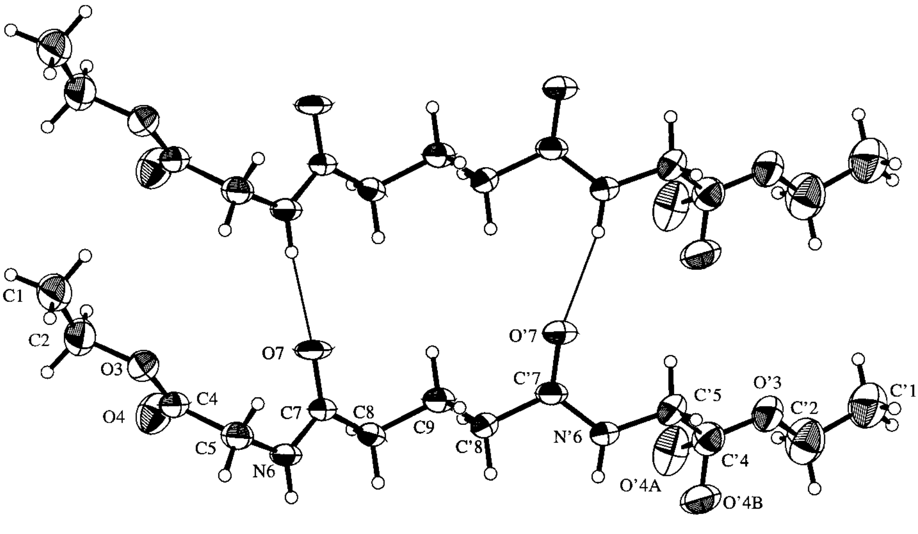

Fig. 1. An ORTEP-II[8] (25% probability ellipsoids) view of the title compound (EtGGGEt) showing the numbering scheme. H atoms are shown as isotropic spheres of arbitrary radii. Two equivalent molecules interacting through two hydrogen bonds (thinner lines) are represented.

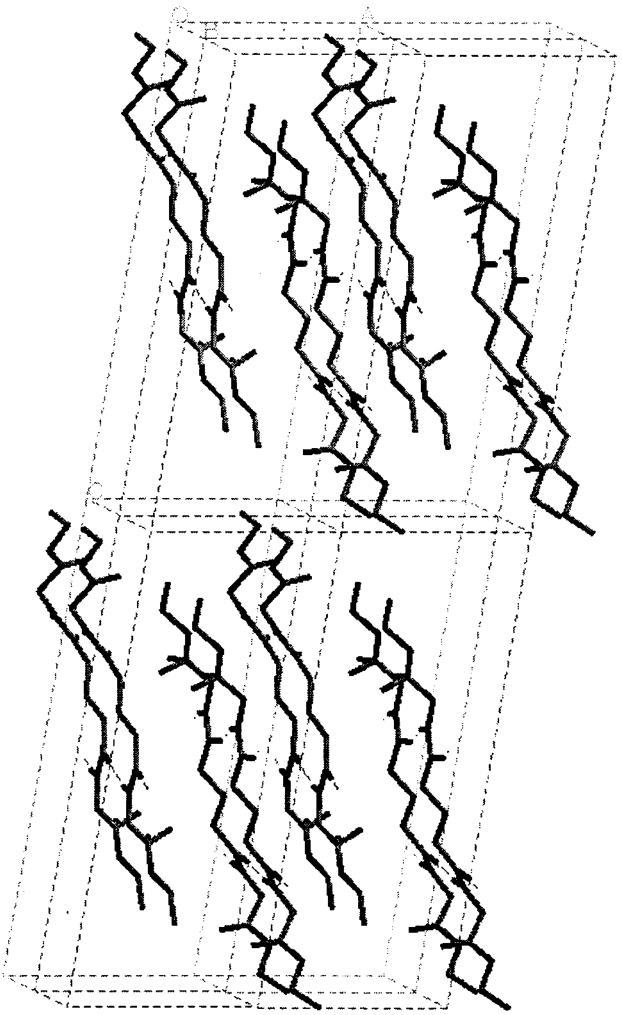

Fig. 2. Crystal packing of the studied compound (EtGGGEt) drawn with the CERIUS 3.1 software package.[9] Molecules are hydrogen bonded along the *b* axis direction. Note the different environment of the two halves of the molecule.

close to that found in EtGSGEt (−156.5 and 73°, respectively to −162 and 72°), the φ torsion angle of the second residue has a deviation toward a skew conformation (−129°). This observation shows a slight deviation from the reported values (68–94° interval) on the $-OCOCH_2NH-$ derivatives that are available in the Cambridge Structure Data Base.[11] In fact, this distortion may be due to the improvement of contacts with the glutaryl residue of a neighboring molecule. Note that this is not the case for the former glycine unit. In the same way, the O′4 carbonyl oxygen atom is disordered in two positions, although they still have close contacts with glutaryl carbon atoms of a neighbor molecule as it is shown in Table 3c. In fact, all the atoms of the second glycine residue (C′1 to N′6) have a bigger temperature factor than the chemically related atoms of the first glycine residue (C1 to N6) (Table 2). Slight differences have also been found in the hydrogen bond geometry that involves both halves of the molecule (Table 3b). The amide groups are planar, with a root-mean square distance of the atoms from the best planes defined by them of 0.005 and 0.023 Å for C5−N6−C7(O7)−C8 and C′5−N′6−C′7(O′7)−C′8, respectively.

The molecular packing is characterized by the establishment of a single hydrogen bond direction between molecules (Fig. 1), in a similar way to that postulated for the γ-form[12] of nylons derived from odd diacids. A twofold screw axis parallel to the hydrogen bond direction relates the non-hydrogen bonded molecules of the unit cell. Thus, all amide groups result with the same orientation and so the crystal has a polar structure (Fig. 2).

Acknowledgments

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