

Table 2. Ring puckering parameters in compound (I)

|                           | $Q$ (Å)   | $\varphi_2$ (°)      |
|---------------------------|-----------|----------------------|
| Ideal values <sup>a</sup> |           |                      |
| Five-membered envelope    | –         | $n \times 36$        |
| Five-membered half-chair  | –         | $(n \times 36) + 18$ |
| Furanoid ring             |           |                      |
| Molecule A                | 0.258 (3) | 223.3 (6)            |
| Molecule B                | 0.272 (3) | 215.8 (6)            |
| Lactone ring              |           |                      |
| Molecule A                | 0.230 (3) | 244.8 (7)            |
| Molecule B                | 0.259 (3) | 251.1 (7)            |

<sup>a</sup> Cremer & Pople (1975).

The origin was fixed according to the method of Flack & Schwarzenbach (1988). The program *PLATON* (Spek, 1998) confirmed that there was no overlooked additional symmetry relating the two independent molecules. All H atoms were placed in geometrically calculated positions. The methyl H atoms were refined as rigid groups, which were allowed to rotate but not to tip, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . All other H atoms were allowed to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *MSCI/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSCI/AFD Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS97* direct methods (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

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## References

- Bandzouzi, A. & Chapleur, Y. (1987a). *Carbohydr. Res.* **171**, 13–24.  
 Bandzouzi, A. & Chapleur, Y. (1987b). *J. Chem. Soc. Perkin Trans.* **1**, pp. 661–664.  
 Brockhaus, M. & Lehmann, J. (1977). *Carbohydr. Res.* **53**, 21–31.  
 Brockhaus, M. & Lehmann, J. (1978). *Carbohydr. Res.* **63**, 301–306.  
 Conde, A., Moreno, E. & Márquez, R. (1980). *Acta Cryst.* **B36**, 1713–1715.  
 Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.  
 Csuk, R. & Glänzer, B. I. (1990). *J. Carbohydr. Chem.* **9**, 797–807.  
 Csuk, R. & Glänzer, B. I. (1991). *Tetrahedron*, **47**, 1655–1664.  
 Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* **A44**, 499–506.  
 Jeffrey, G. A., Rosenstein, R. D. & Vlasse, M. (1967). *Acta Cryst.* **22**, 725–733.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Kim, S. H., Jeffrey, G. A., Rosenstein, R. D. & Corfield, P. W. R. (1967). *Acta Cryst.* **22**, 733–743.  
 Lehmann, J. & Schwesinger, B. (1982a). *Carbohydr. Res.* **107**, 43–53.  
 Lehmann, J. & Schwesinger, B. (1982b). *Carbohydr. Res.* **110**, 181–185.  
 Li, X. (1998). MSc thesis, National University of Singapore, Singapore.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1991). *MSCI/AFD Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1997a). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1997b). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1998). *PLATON. Program for the Analysis of Molecular Geometry*. Version of July 1998. University of Utrecht, The Netherlands.

Usher, J. J. & English, R. B. (1978). *Acta Cryst.* **B34**, 2012–2014.

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## Amino-11-undecanoic acid cyclic dimer hydrochloride†

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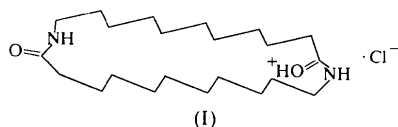
## Abstract

The structure of the hydrochloride salt of amino-11-undecanoic acid cyclic dimer (C<sub>22</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub>·HCl) corresponds to two monomeric units of nylon 11. The intensity data were collected at 203 K. Two molecules are linked by two short hydrogen bonds with O···O distances of 2.406(6) and 2.464(6) Å between half-protonated amide-O atoms. The methylene groups are all-*trans* except for two terminal groups, which display a (–)synclinal form (*gauche*). The ring is closed through bent amide groups, which are reminiscent of β-turns in proteins. The all-*trans* methylene chains along both sides of the ring are not parallel, but are organized at an angle of about 10.9(6)°.

## Comment

We have determined the structure of a 24-atom ring made up of two units of aminoundecanoic acid, (I). This is part of a research effort aimed at understanding folding in polyamides (nylons) and in related compounds like proteins.

† IUPAC name: 1,13-diazatetracos-2,14-dioxonium chloride.



Two molecules related by a twofold axis are linked by two strong hydrogen bonds involving the half-protonated amide-O atoms. The amide-N atoms participate in intermolecular hydrogen bonds as donors with chloride anions as acceptors producing an infinite three-dimensional framework, which contrasts with the pattern found in other hydrochloride lactams with the protonation at the O atom (Winkler & Dunitz, 1975), where the hydrogen bonds produce infinite chains. The C22—N1—C1—O1 and C11—N2—C12—O2 torsion angles display a *cis* form typical for lactams with a ring containing more than nine atoms. The hemiprotonation of the amide groups results in a modification of the bond distances in the peptide group, which increments some of its double-bond character, as shown by the shorter C—N distances [mean value: 1.222 (9) Å], which in standard peptides is about 1.32 Å. Each methylene chain in the ring has an *anti*-periplanar form (*trans* form) except for C1—C2—C3—C4 and C12—C13—C14—C15 which display a (–)synclinal form (*gauche*). The turn of the chain takes place at the amide group in a way similar to that observed in proteins, although the torsion angles are different. The methylenic chains along both sides of the ring are not parallel, they are organized at an angle of 10.9(6)°. It is interesting that the ring we present in this work shows turns in the peptide

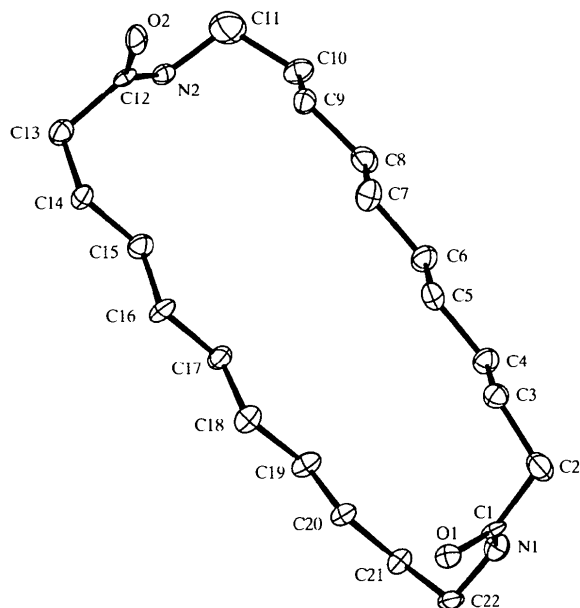


Fig. 1. Molecular structure of (I) showing 50% probability displacement ellipsoids and atom-numbering scheme. The Cl atom has been omitted.

moiety which may also be a general feature in the case of lamellar folding in nylon crystals.

Cycloalkanes of a similar size (Groth, 1979) have a similar conformation, except for the angles equivalent to  $\varphi$  (C1—N1—C22—C21 and C12—N2—C11—C10) and  $\psi$  (N1—C1—C2—C3 and N2—C12—C13—C14) which are in the *gauche* region (about 60°). Thus, cycloalkanes achieve folding by two consecutive *gauche* angles which are of the same sign, whereas in the title compound we have a *gauche* angle next to the  $\varphi/\psi$  angles of about 106°, as shown in Table 1.

## Experimental

The title compound was isolated from the by-products obtained in the industrial synthesis of nylon 11 (Rilsan). The monomeric and cyclic oligomers in the polymer were extracted by boiling in methanol for 24 h. The cyclic dimer was purified by liquid chromatography (semi-preparative HPLC, Spherisorb C18, 250×20 mm S5 ODS 2, mobile phase: acetic acid 5 mM/methanol = 20:80, flow rate: 7 ml min<sup>-1</sup>, detection: UV 210 nm). The peaks were identified as the monomer, dimer and trimer by mass spectroscopy.

Hexagonal prismatic crystals, with well developed features were grown by the sitting-drop vapour-phase diffusion method from a mixture of ethyl acetate and 2-chloroethanol. Due to the high instability of the crystals, reflections were collected at 203 K.

### Crystal data

C<sub>22</sub>H<sub>43</sub>N<sub>2</sub>O<sub>2</sub>·Cl<sup>-</sup>  
*M<sub>r</sub>* = 403.03  
 Orthorhombic  
*F*2*dd*  
*a* = 14.627 (3) Å  
*b* = 15.834 (4) Å  
*c* = 43.135 (13) Å  
*V* = 9990 (4) Å<sup>3</sup>  
*Z* = 16  
*D<sub>s</sub>* = 1.072 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 8–14°  
 $\mu$  = 0.170 mm<sup>-1</sup>  
*T* = 203 (1) K  
 Prism  
 0.3 × 0.2 × 0.2 mm  
 Colourless

### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: none  
 6736 measured reflections  
 2296 independent reflections  
 (plus 1646 Friedel-related reflections)  
 1669 reflections with  
 $I > 2\sigma(I)$

*R*<sub>int</sub> = 0.037  
 $\theta_{\max}$  = 25.01°  
 $h = -17 \rightarrow 16$   
 $k = 0 \rightarrow 18$   
 $l = 0 \rightarrow 51$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.197$   
 $S = 0.847$   
 3942 reflections  
 247 parameters

$\Delta\rho_{\max} = 0.368 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.222 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

H atoms: see text  
 $w = 1/[\sigma^2(F_o^2) + (0.0904P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.004$

Absolute structure: Flack  
 (1983)  
 Flack parameter = 0.11 (18)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1071). Services for accessing these data are described at the back of the journal.

Table 1. Selected geometric parameters (Å, °)

|                |           |                 |           |
|----------------|-----------|-----------------|-----------|
| O1—C1          | 1.268 (6) | N1—C22          | 1.450 (8) |
| O2—C12         | 1.285 (7) | N2—C12          | 1.241 (6) |
| N1—C1          | 1.202 (7) | N2—C11          | 1.453 (9) |
| C1—N1—C22      | 124.7 (6) | N2—C11—C10      | 113.0 (7) |
| C12—N2—C11     | 120.8 (6) | N2—C12—O2       | 123.6 (6) |
| N1—C1—O1       | 123.2 (6) | N2—C12—C13      | 118.5 (6) |
| N1—C1—C2       | 122.4 (6) | O2—C12—C13      | 117.8 (5) |
| O1—C1—C2       | 114.2 (6) | N1—C22—C21      | 108.0 (6) |
| C22—N1—C1—O1   | -0.9 (11) | C11—N2—C12—O2   | 2.6 (10)  |
| N1—C1—C2—C3    | 97.3 (8)  | N2—C12—C13—C14  | 106.3 (7) |
| O1—C1—C2—C3    | -77.1 (8) | O2—C12—C13—C14  | -70.5 (7) |
| C1—C2—C3—C4    | -74.4 (8) | C12—C13—C14—C15 | -73.6 (7) |
| C12—N2—C11—C10 | 108.8 (8) | C1—N1—C22—C21   | 109.4 (8) |
| C9—C10—C11—N2  | -72.2 (8) | C20—C21—C22—N1  | -69.2 (7) |

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

| D—H...A                    | D—H       | H...A     | D...A     | D—H...A   |
|----------------------------|-----------|-----------|-----------|-----------|
| N1—H1N...Cl <sup>i</sup>   | 0.862     | 2.262     | 3.116 (6) | 170.7     |
| N2—H2N...Cl <sup>ii</sup>  | 0.858     | 2.215     | 3.071 (5) | 175.4     |
| O2—H2O...O2 <sup>iii</sup> | 1.206 (4) | 1.206 (4) | 2.406 (6) | 171.9 (3) |
| O1—H1O...O1 <sup>iii</sup> | 1.232 (4) | 1.232 (4) | 2.464 (6) | 180.0 (6) |

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

Two octants of reflections were measured in order to ameliorate the collected intensity values and they were sorted and merged before the structure solution and refinement.

All non-H atoms were refined anisotropically. The hydroxy-H atoms were located on the twofold axis in the middle of the hydrogen bonds linking two molecules. Attempts to define and refine disordered H-atom positions at the more usual O—H distance of 0.84 Å failed with the H atoms always returning to the twofold axis. This result is supported by the data in the Cambridge Structural Database (Allen & Kennard, 1993), where some 114 O—H distances are close to 1.23 Å when the O...O hydrogen-bonding distance is less than 2.5 Å (from 139 observations). It occurs, for example, in glyoximate or dihydrogenphosphato ions, where disorder of the H atom gives a symmetric hydrogen bond with a very long O—H distance. The positions of the (N)H and (C)H atoms were computed geometrically and refined using a riding model. An overall isotropic temperature factor was assumed for all H atoms. The polar-axis direction has been chosen arbitrarily as the standard uncertainty in the Flack parameter makes the result inconclusive.

Data collection: *CAD-4/PC* (Kretschmar, 1996). Cell refinement: *CAD-4/PC*. Data reduction: *CFEO* (Solans, 1978). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP3.2* (Brueggemann & Schmid, 1990). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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## References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Brueggemann, R. & Schmid, G. (1990). PC version of *ORTEP3.2*. University of Ulm, Germany.
- Groth, P. (1979). *Acta Chem. Scand. Ser. A*, **33**, 199–201.
- Kretschmar, M. (1996). *CAD-4/PC*. Version 2.0. PC Version of *CAD-4* Version 5.0. University of Tübingen, Germany.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Solans, X. (1978). *CFEO*. University of Barcelona, Spain.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Winkler, F. K. & Dunitz, J. D. (1975). *Acta Cryst.* **B31**, 273–275, 278–281.

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## 3-Triphenylphosphoniopropionate dihydrate

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## Abstract

Zwitterionic 3-triphenylphosphoniopropionate crystallizes as a dihydrate, C<sub>21</sub>H<sub>19</sub>O<sub>2</sub>P·2H<sub>2</sub>O, in which the carboxyl-O atoms are each hydrogen-bonded to a water molecule.

## Comment

Betaine, [(CH<sub>3</sub>)<sub>3</sub>NCH<sub>2</sub>CO<sub>2</sub>], and its analogs react with copper salts to furnish copper complexes that are rich in carboxylate ligands (Chen & Mak, 1994). Copper perchlorate forms tetrakisbetainecopper perchlorate with betaine (Ng *et al.*, 1998); the pyridiniopropionate homolog (Chen & Mak, 1992) reacts with lanthanum perchlorate to yield novel octadecanuclear copper(II)–lanthanoid(III) clusters (Chen *et al.*, 1996). The tertiary phosphine betaines, which can be synthesized by the carboxyalkylation of tertiary phosphines, are the phosphorus analogs of these tertiary amine betaines. Furthermore, owing to the presence of four P—C bonds, such compounds are expected