

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (2)

O1—C15	1.318 (2)	C2—C3	1.497 (2)
O2—C15	1.222 (2)	C3—C4	1.336 (2)
C1—C2	1.515 (3)	C4—C12	1.483 (2)
C1—C11	1.516 (3)	C4—C15	1.479 (2)
C2—C1—C11	110.4 (2)	C4—C12—C11	116.8 (1)
C1—C2—C3	108.1 (2)	O1—C15—O2	122.9 (1)
C2—C3—C4	119.6 (2)	O1—C15—C4	115.2 (1)
C3—C4—C12	120.0 (2)	O2—C15—C4	121.8 (1)
C1—C11—C12	118.3 (2)		

Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
(1)				
O1—H4 $\cdots$ O2 <sup>i</sup>	1.22 (4)	1.42 (4)	2.634 (2)	176 (3)
(2)				
O1—H4 $\cdots$ O2 <sup>ii</sup>	0.99 (2)	1.66 (2)	2.651 (2)	173 (2)

Symmetry codes: (i)  $-x, -y, 1-z$ ; (ii)  $1-x, 1-y, -z$ .

Scan widths were  $(1.50 + 0.35\tan\theta)$  and  $(1.10 + 0.35\tan\theta)^\circ$  in  $\omega$  for (1) and (2), respectively. Background/scan time-ratios were 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignments, systematic absences and intensity statistics consistent with centrosymmetry indicated space group  $P2_1/n$  (No. 14) for (1), and space group  $Pbca$  (No. 61) for (2); since refinement proceeded well they were adopted. Difference Fourier methods were used to locate the initial H-atom positions. In later stages of refinement for (1), all H atoms except the carboxy H atom, H4, were made canonical, with C—H distances of 0.98  $\text{\AA}$  and with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  of the attached C atom. The carboxy H atom was refined isotropically. In later stages of refinement for (2), atoms H5—H10 were made canonical as described above, while the remaining six H atoms were refined isotropically; the refined C—H distances ranged from 0.98 (2) to 1.03 (2)  $\text{\AA}$ , with a mean value of 1.00 (1)  $\text{\AA}$ . When molecule (1) was initially refined on  $F$ , the three leading residual peaks in a difference Fourier map had locations suggestive of a (somewhat distorted) carboxy group on ring atom C5. Atom names C15B, O1B and O2B were assigned to these peaks; C15B was moved toward C5 along the ray connecting them until their separation matched the C4—C15 distance, at which point the position of C15B was fixed. Also the isotropic displacement parameters for these atoms were fixed at the values found for the corresponding ordered atoms. The occupancies of the two sites were then refined along with the coordinates of O1B and O2B. Since the refined value of the disordered site occupancy is only 0.045 (2), the contribution of the disordered atoms to the overall fit is small. However, the model with disorder is statistically superior, on the basis of the Hamilton ratio test (Hamilton, 1965), to the alternative model without disorder at the  $\alpha = 0.005$  level of significance. Although the refined values of the C15B to O1B and O2B distances are somewhat larger than the corresponding values for the ordered molecule, further modeling was not pursued. For (1), the maximum effect of extinction was 2.2% of  $F_o$  for 022; for (2), an extinction coefficient was not refined since the predicted value was negative. The maximum positive residual peak was located 1.42  $\text{\AA}$  from C10 for (1) and 0.92  $\text{\AA}$  from C5 for (2); the maximum negative peak was located 1.76  $\text{\AA}$  from C8 for (1) and 1.14  $\text{\AA}$  from C2 for (2).

For both compounds, data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation,

1988); cell refinement: *MSCIAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

We gratefully acknowledge support for LJF by PPG, Inc. We thank Dr Kurt Loening for his help with nomenclature and Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1359). Services for accessing these data are described at the back of the journal.

## References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Fitzgerald, L. J. & Gerkin, R. E. (1997). *Acta Cryst.* **C53**, 1265–1267.
- Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*. Version 5.0. Molecular Structure Corporation, The Woodlands, TX 77381, USA.
- Sheldrick, G. M. (1985). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard. Oxford University Press.
- Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
- Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

*Acta Cryst.* (1998). **C54**, 969–972

## 8-Aminocaprylic Acid

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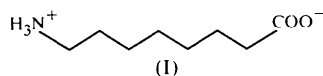
## Abstract

The title acid, 8-aminoctanoic acid,  $\text{C}_8\text{H}_{17}\text{NO}_2$ , crystallized in the centrosymmetric space group  $P2_1/n$  in the zwitterionic form. The three H atoms involved in

hydrogen bonding are ordered. The five intermolecular N—H···O hydrogen bonds have N···O distances ranging from 2.752 (2) to 3.258 (2) Å and N—H···O angles ranging from 131 (2) to 165 (2)°. Each molecule is linked to six neighboring molecules by a total of ten hydrogen bonds. A complex network of hydrogen bonds ensues in which chains predominate.

### Comment

This report on 8-aminocaprylic acid is one of a series on hydrogen bonding in amino-substituted carboxylic acids, and follows a report on a novel tetragonal phase of  $\gamma$ -aminobutyric acid (Dobson & Gerkin, 1996). The title acid crystallized in the centrosymmetric space group  $P2_1/n$  as a zwitterion, (I), the carboxyl proton having been transferred to the N atom. The refined mol-



ecule is shown in Fig. 1, together with the numbering scheme. As a consequence of the proton transfer, cyclic carboxylic acid group hydrogen-bonded dimers are not possible. However, both hydrogen-bond chains and hydrogen-bond cycles are formed, which involve the carboxylate O atoms as acceptors and the protonated amino N atom as donor. In this structure, each molecule is linked to six neighbors by a total of ten hydrogen bonds, in five of which it acts as donor and in the other five as acceptor. The geometric details of these bonds are given in Table 2; the criteria for inclusion in this table are that the donor···acceptor distance is less than 3.3 Å and that the H atom involved is at least as close to the acceptor atom as the donor atom is. The ten hydrogen bonds involving the homebase molecule are depicted in Fig. 2, which upon brief inspection makes apparent the basis for the complex network of hydrogen bonds in this structure. The results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) involving these five hydrogen bonds (for this purpose designated *a* to *e*, in the order given in Table 2) for the first- and basic second-level graph sets, are presented in Table 3. This tabulation shows the predominance of chains among the hydrogen-bonding patterns. These 13 chains propagate variously along *a* (2), *b* (7), [101] (3) and [10 $\bar{1}$ ] (1). It may be noted that no chain propagates along *c* although, due to the substantial difference in the *a* and *c* axial lengths, this might appear to be the case upon a cursory view of Fig. 2. The four ring patterns are apparent in Fig. 2; the first-level [ $R_2^2(22)$ ] rings occur about centers of symmetry while the remaining rings do not.

Distances and angles of special interest in the title molecule are given in Table 1. Among the most comparable molecules for structural comparisons are  $\gamma$ -aminobutyric acid (Dobson & Gerkin, 1996) and

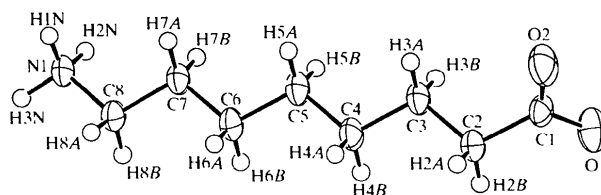


Fig. 1. ORTEPII (Johnson, 1976) drawing of 8-aminocaprylic acid showing the atomic numbering scheme. Displacement ellipsoids are drawn for 50% probability for all atoms except H atoms, for which they have been set artificially small.

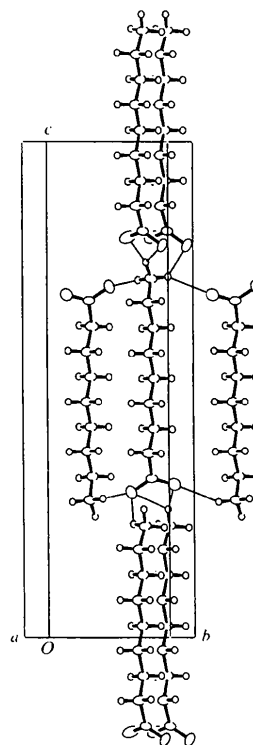


Fig. 2. ORTEPII (Johnson, 1976) diagram of a central 8-aminocaprylic acid molecule and the six molecules to which it is directly hydrogen bonded. Displacement ellipsoids are drawn for 50% probability for all atoms except H atoms, for which they have been set artificially small. Intermolecular hydrogen bonds are shown as narrow lines.

7-oxo-7-(phenylamino)heptanoic acid (Feeder & Jones, 1994). Whereas  $\gamma$ -aminobutyric acid is partially folded and zwitterionic, the title acid is extended and zwitterionic, while the substituted heptanoic acid is extended but not zwitterionic. Since in the heptanoic acid a neutral carboxyl group is present, while in the butyric acid and the title acid a carboxylate ion is present, the C1—C2 (present numbering) bond length may reflect this; the observed values are 1.483 (3), 1.519 (4) and 1.520 (2) Å, respectively. However, for the heptanoic acid and the title acid, bonds C2—C3 through C5—C6 (present numbering) appear to be quite similar; the mean values are 1.510 (3) and 1.520 (2) Å, respectively. Further, the C—C—C bond angles in the chains (C1—C2—C3

through C5—C6—C7 in the present numbering) are quite comparable, the average values being 114.0(16) and 113.7(4)°, respectively. Consistent with the s.u.'s for the angular means, the values for the heptanoic acid have a range of 4.0°, but for the title acid a range of only 1.1°.

The closest intermolecular approaches in this structure, excluding pairs of atoms in groups hydrogen bonded to each other, are at least 0.02 Å greater than the corresponding Bondi (1964) van der Waals radius sums. Among the structures we have determined, this is an uncommon occurrence. It highlights the dominant role hydrogen bonding plays in the organization of this structure.

## Experimental

8-Aminocaprylic acid was obtained as a white crystalline powder from the Aldrich Chemical Company. This solid was dissolved in water at room temperature and the solution was filtered. Room-temperature evaporation of the filtrate produced thick slabs, one of which was cut to provide the experimental sample.

### Crystal data

C<sub>8</sub>H<sub>17</sub>NO<sub>2</sub>  
*M<sub>r</sub>* = 159.23  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 4.615 (1) Å  
*b* = 7.519 (1) Å  
*c* = 24.970 (1) Å  
 $\beta$  = 90.65 (2)°  
*V* = 866.3 (3) Å<sup>3</sup>  
*Z* = 4  
*D<sub>r</sub>* = 1.221 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

### Data collection

AFC-5S diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 2407 measured reflections  
 1997 independent reflections  
 1344 reflections with  
 $I > 2\sigma(I)$   
*R<sub>int</sub>* = 0.013  
 $\theta_{\max}$  = 27.56°

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.051  
*wR*(*F*<sup>2</sup>) = 0.074  
*S* = 3.16  
 1997 reflections  
 169 parameters  
 All H atoms refined  
 $w = 1/\sigma^2(F^2)$   
 $(\Delta/\sigma)_{\max} < 0.01$

Mo *K*α radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 25 reflections  
 $\theta = 13.2$ – $17.4$ °  
 $\mu = 0.081$  mm<sup>-1</sup>  
*T* = 296 K  
 Cut slab  
 0.38 × 0.35 × 0.27 mm  
 Colorless

*h* = 0 → 6  
*k* = 0 → 9  
*l* = -32 → 32  
 6 standard reflections every 150 reflections  
 intensity variation: ±1.6% (average maximum relative intensity)

$\Delta\rho_{\max} = 0.46$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.36$  e Å<sup>-3</sup>  
 Extinction correction: Zachariasen (1963, 1968)  
 Extinction coefficient:  $6.8(10) \times 10^{-7}$   
 Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, N, O)

Table 1. Selected geometric parameters (Å, °)

O1—C1	1.248 (2)	N1—C8	1.486 (2)
O2—C1	1.238 (2)		
O1—C1—O2	123.9 (2)	O2—C1—C2	118.1 (2)
O1—C1—C2	118.0 (2)	N1—C8—C7	111.3 (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—H1N...O1 <sup>i</sup>	0.93 (2)	2.31 (2)	3.004 (2)	131 (2)
N1—H1N...O2 <sup>ii</sup>	0.93 (2)	2.48 (2)	3.178 (2)	133 (2)
N1—H2N...O1 <sup>iii</sup>	1.03 (2)	1.80 (2)	2.809 (2)	164 (2)
N1—H3N...O2 <sup>iv</sup>	1.01 (2)	1.76 (2)	2.752 (2)	165 (2)
N1—H3N...O1 <sup>v</sup>	1.01 (2)	2.50 (2)	3.258 (2)	132 (1)

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

Table 3. First- and basic second-level graph-set descriptors involving hydrogen bonds, designated *a*–*e*, in the order given in Table 2

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
<i>a</i>	C(11)	C <sub>2</sub> <sup>1</sup> (4)	C <sub>3</sub> <sup>1</sup> (4)	C <sub>3</sub> <sup>2</sup> (6)	C <sub>3</sub> <sup>1</sup> (4)
<i>b</i>		R <sub>2</sub> <sup>2</sup> (22)	C <sub>3</sub> <sup>2</sup> (6) R <sub>3</sub> <sup>2</sup> (28)	C <sub>3</sub> <sup>1</sup> (4)	C <sub>3</sub> <sup>2</sup> (6)
<i>c</i>			R <sub>3</sub> <sup>2</sup> (22)	C <sub>3</sub> <sup>2</sup> (6)	C <sub>3</sub> <sup>1</sup> (4)
<i>d</i>				C(11)	C <sub>3</sub> <sup>1</sup> (11) R <sub>3</sub> <sup>2</sup> (4)
<i>e</i>					C(11)

Scan widths were  $(1.60 + 0.35\tan\theta)^\circ$  in  $\omega$ , with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and centrosymmetric intensity statistics indicated space group *P*2<sub>1</sub>/*n* (No. 14); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions and the H atoms were then refined isotropically. The refined C—H distances ranged from 0.95 (2) to 1.00 (2) Å with a mean value 0.97 (2) Å; refined N—H distances are given in Table 2. The maximum effect of extinction is 4.1% of *F<sub>o</sub>* for O20. The maximum positive residual peak was located ~1.0 Å from O1 and 1.2 Å from C1; the maximum negative peak was located ~0.6 Å from O2.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1103). Services for accessing these data are described at the back of the journal.

## References

- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.  
 Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.  
 Creagh, D. C. & McAuley, W. J. (1992). *International Tables for Crystallography*, Vol. C, pp. 219–222. Dordrecht: Kluwer Academic Publishers.

- Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* **C52**, 3075–3078.
- Feeder, N. & Jones, W. (1994). *Acta Cryst.* **C50**, 1732–1734.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
- Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
- Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

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### DL-3-Aminoisobutyric Acid Monohydrate

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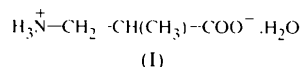
#### Abstract

The title acid, 3-amino-2-methylpropanoic acid monohydrate, C<sub>4</sub>H<sub>9</sub>NO<sub>2</sub>·H<sub>2</sub>O, crystallized in the centrosymmetric space group *Pbca* in the zwitterionic form. The three H atoms on N, which are involved in hydrogen bonding, are ordered. The three intermolecular N—H···O hydrogen bonds have N···O distances ranging from 2.758(2) to 2.809(2) Å and N—H···O angles ranging from 149(2) to 171(1)°. The two intermolecular O—H···O hydrogen bonds have O···O distances 2.739(2) and 2.755(2) Å, and O—H···O angles 170(2) and 175(2)°. Each acid molecule and its associated water molecule are directly hydrogen bonded to five acid molecules and two water molecules; the structure comprises two subsets of molecules which are not cross-linked by these hydrogen bonds. Through basic second-level graphs, approximately two-thirds of the hydrogen-bonding patterns are finite and one-third are chains; there is a single ring pattern, which occurs about a center of symmetry.

#### Comment

This report on DL-3-aminoisobutyric acid monohydrate is one of a series on hydrogen bonding in amino-substituted carboxylic acids, and follows reports on a

novel tetragonal phase of  $\gamma$ -aminobutyric acid and on 8-aminocaprylic acid (Dobson & Gerkin, 1996, 1998). The title acid crystallized in the centrosymmetric space group *Pbca* as a zwitterion, (I), the carboxyl proton having been transferred to the N atom. The refined mol-



ecule, and the associated water molecule given in the atom list, are shown in Fig. 1, together with the atomic numbering scheme. As a consequence of the proton transfer, cyclic carboxylic acid group hydrogen-bonded dimers are not possible. Each potential acceptor atom (O1, O2, O3) and each potential H-atom participant (H1N, H2N, H3N, H1O, H2O) is involved in hydrogen bonding. In this structure, each acid molecule and its associated water molecule are directly hydrogen bonded to five acid molecules and two water molecules. The structure comprises two subsets of molecules which are not cross-linked by hydrogen bonds: molecules related by symmetry operations 1, 3, 5 and 7, and translations form one subset, while those related by 2, 4, 6 and 8, and translations form the other. The geometric details of the five hydrogen bonds are given in Table 2. The results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995), involving the five hydrogen bonds (for this purpose designated *a* to *e*, in the order given in Table 2) for the first- and basic second-level graph sets, are presented in Table 3. This tabulation shows the predominance of finite patterns and chains among the hydrogen-bonding patterns. The five chains propagate along **b** (1) or **c** (4). The nine hydrogen bonds involving the homebase molecule and its associated water molecule are depicted and labeled in Fig. 2. The single ring pattern, which occurs about a center of symmetry, is apparent in Fig. 2.

It should be noted that there are six additional hydrogen bonds having donor···acceptor distances very slightly greater than our customary cutoff (3.3 Å), but substantially greater than those included in Table 2, and having angles in the range 89–119°: these are N1—H1N···O3<sup>iii</sup> and N1—H3N···O3<sup>iii</sup>, N1—H1N···O2<sup>v</sup> and N1—H2N···O2<sup>v</sup>, and O3—H1O···N1<sup>iii</sup> and O3—H2O···N1<sup>iii</sup> [symmetry codes: (iii) 1 - x, 1 - y, 1 - z; (v) 1 - x,  $\frac{1}{2} + y, \frac{1}{2} - z$ ]. These bonds make a secondary contribution to the structure.

Distances and angles of special interest in the title molecule are given in Table 1. Among the most comparable molecules for structural comparisons are  $\gamma$ -aminobutyric acid (Dobson & Gerkin, 1996), 8-aminocaprylic acid (Dobson & Gerkin, 1998) and 7-oxo-7-(phenylamino)heptanoic acid (Feeder & Jones, 1994). Whereas  $\gamma$ -aminobutyric acid and the title acid are partially folded and zwitterionic, the 8-aminocaprylic acid is extended and zwitterionic, while the substituted hep-