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Azetidine, pyrrolidine and hexamethyleneimine at 170 K

Andrew D. Bond, a, * John E. Davies b and Simon Parsons c

a University of Southern Denmark, Department of Physics and Chemistry, Campusvej 55, 5230 Odense M, Denmark, b Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England, and c School of Chemistry, University of Edinburgh, King’s Buildings, West Mains Road, Edinburgh EH9 3JJ, Scotland

Correspondence e-mail: adb@chem.sdu.dk

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The crystal structures of the cyclic amines azetidine (C3H7N), pyrrolidine (C4H9N) and hexamethyleneimine (homopiperidine, C6H13N), of the series (CH2)nNH, with n = 3, 4 and 6, respectively, have been determined at 170 K, following in situ crystallization from the melt. These structures provide crystallographic data to complete the homologous series of cyclic amines (CH2)nNH, for n = 2–6. Azetidine and pyrrolidine contain chains propagating along 21 screw axes, in which the molecules are linked by co-operative N—H· · ·C—H hydrogen bonds. Azetidine has two molecules in its asymmetric unit, while pyrrolidine has only one. Hexamethyleneimine contains tetrameric hydrogen-bonded rings formed about crystallographic inversion centres, with two molecules in its asymmetric unit. The observation of crystallographically distinct molecules in the hydrogen-bonded chains of azetidine and cyclic hydrogen-bonded motifs in hexamethyleneimine is consistent with expectations derived from comparison with monoalcohols forming chains or rings by co-operative O—H· · ·H hydrogen bonds. The next member of the cyclic amine series, heptamethyleneimine, forms a cubic plastic phase on cooling from the melt.

Comment

Contemporary developments in instrumentation and techniques for in situ crystallization have greatly simplified the task of obtaining diffraction data for low-melting materials (Boese & Nussbaumer, 1994; Davies & Bond, 2001). This paper describes single-crystal X-ray structures for the cyclic amines azetidine, (I), pyrrolidine, (II), and hexamethyleneimine (homopiperidine), (III), all of which are liquid under ambient conditions. Together with the previously reported structures of aziridine (Mitzel et al., 1997) and piperazine (Parkin et al., 2004), these structures provide crystallographic data to complete the homologous series of cyclic amines (CH2)nNH, for n = 2–6.

In each structure of the series, molecules are linked by co-operative N—H· · ·N hydrogen bonds with comparable geometric characteristics (Tables 1–3). Aziridine (n = 2), azetidine (n = 3; Fig. 1), pyrrolidine (n = 4; Fig. 2) and piperazine (n = 5) all form one-dimensional hydrogen-bonded chains. In these last two structures, the chains propagate along 21 screw axes in the space group P21/c, with one molecule in the asymmetric unit (Fig. 3). In azetidine, the chains also propagate along 21 screw axes in P21/c, but with two crystallographically distinct molecules in each chain (Fig. 4). Thus, every second molecule along the chain is related by the 21 screw operation, and every fourth molecule is related by translation along b. Aziridine crystallizes in the space group P1 with three crystallographically distinct molecules in each hydrogen-bonded chain. The chain conformation has approximate 31 screw symmetry (Fig. 5), with every third molecule related by translation along b. In hexamethyleneimine (Fig. 6), the molecules form tetrameric rings with a closed cycle of co-operative N—H· · ·N hydrogen bonds. The rings are formed about crystallographic inversion centres in the space group P21/n, with two of the four molecules of the tetramer being crystallographically distinct (Fig. 7).

Figure 1
The two molecules in the asymmetric unit of azetidine, (I), with displacement ellipsoids drawn at the 50% probability level, except for H atoms bound to C atoms, which are shown as small spheres of arbitrary radii.

Figure 2
The molecular structure of pyrrolidine, (II), with displacement ellipsoids drawn at the 50% probability level, except for H atoms bound to C atoms, which are shown as small spheres of arbitrary radii.
The N—H···N hydrogen-bond motifs in the cyclic amines are reminiscent of those observed frequently in monoalcohols. For example, hydrogen-bonded chains exist in both the ambient-pressure (Jönsson, 1976) and high-pressure (Allan & Clark, 1999) polymorphs of ethanol, while the more bulky 3-ethyl-3-pentanol forms cyclic tetramers (Bond, 2006). The NH group resembles the OH group in that it can act simultaneously as a hydrogen-bond donor (albeit a worse one than OH; Steiner, 2002) and as an acceptor. Thus, extended chains and closed rings are expected motifs in both cases. For the monoalcohols, Brock & Duncan (1994) noted that the occurrence of structures with more than one crystallographically distinct molecule is anomalously high on account of frequent conflicts between the spatial requirements of O—H···O hydrogen bonds and the overall contraints of molecular close packing, i.e. that molecules are most often arranged about inversion centres, 21 screw axes or glide planes. Formation of extended O—H···O hydrogen-bonded chains in the monoalcohols requires that the O atoms are brought within ca 2.7–2.9 Å of each other. In the cyclic amines, the corresponding N···N distance is slightly longer (ca 3.1–3.2 Å). Within these contraints, O—H···O or N—H···N hydrogen-bonded chains might be compatible with molecular packing about 21 screw axes or glide planes, for example, as in pyrrolidine and piperazine. In other cases, however, such compatibility may not be assured, and the chain motifs are therefore much more likely [compared with structures in the Cambridge Structural Database (Allen, 2002) as a whole] to be formed either with more than one crystallographically distinct molecule, as in azetidine, or around screw or roto-inversion axes of order 3, 4 or 6, as approximated by aziridine. For more bulky molecules, cyclic motifs offer a further alternative. These are commonly tetrameric and may be formed in tetragonal space groups (e.g. 2-phenyladamantan-2-ol; Singelenberg & van Eijck, 1987) or about inversion centres with two crystallographically distinct molecules, as in hexamethyleneimine and 3-ethyl-3-pentanol (Bond, 2006). It has been observed that the packing arrangements of bulky alcohols can be made to resemble those of smaller alcohols on application of increased pressure. For example, the crystal structures of 2-chlorophenol and 4-fluorophenol at ambient pressure contain hydrogen-bonded chains propagating along 32 and 3 axes, respectively, while at high pressure both contain chains along 21 axes (Oswald et al., 2005).

**Figure 3**
A view of pyrrolidine along the c axis, showing two chains linked by cooperative N—H···N hydrogen bonds (dashed lines) propagating along 21 screw axes parallel to the b axis. H atoms bound to C atoms have been omitted. [Symmetry code: (i) −x, y − 1/2, −z + 1/2]

**Figure 4**
A view of azetidine along the c axis, showing one chain linked by cooperative N—H···N hydrogen bonds (dashed lines) propagating along a 21 screw axis parallel to the b axis. The two crystallographically distinct molecules and their symmetry equivalents are distinguished by their shading. H atoms bound to C atoms have been omitted. [Symmetry codes: (i) −x + 1, y − 1/2, −z + 1/2; (ii) −x + 1, y + 1/2, −z + 1/2]

**Figure 5**
Perpendicular views of the hydrogen-bonded chains in aziridine (Mitzel et al., 1997), showing the approximate 31 screw symmetry. The three crystallographically distinct molecules and their symmetry equivalents are distinguished by their shading. H atoms bound to C atoms have been omitted.

**Figure 6**
The two molecules in the asymmetric unit of hexamethyleneimine, (III), with displacement ellipsoids drawn at the 50% probability level, except for H atoms bound to C atoms, which are shown as small spheres of arbitrary radii.
The crystal structure of azetidine was used as a target in the third blind test of crystal structure prediction (CSP2004) organized by the Cambridge Crystallographic Data Centre (Day et al., 2005). The two crystallographically distinct molecules provided difficulty in this exercise, and the correct structure was not present amongst the first three predictions of any of the participants. It was noted that the structure at 170 K appears to be a saddle point on the potential energy surface, which seems to have little influence on the final refined parameters (Görbitz, 1999). Following data collection at 170 K, further cooling of the crystals caused deterioration of the peak shapes for all three compounds, to the extent that no further useful data could be obtained. Attempts were made to crystalize the next member of the series, heptamethylenimine, but this forms a plastic phase on cooling from the melt. The diffraction pattern could be indexed on the basis of a cubic lattice with dimension 11.647 (3) Å, but it was not possible to establish any definite structural model.

Experimental

Single crystals of pyrrolidine and hexamethyleneimine were grown in 0.3 mm diameter glass capillaries at a temperature just below the melting point of the sample, using the manual zone-refinement technique described by Davies & Bond (2001). The diffraction patterns were indexed at a temperature just below the melting point, using the manual zone-refinement technique described by Davies & Bond (2001). The diffraction pattern could be indexed on the basis of numerous partially overlapping components. It was not possible to grow suitable crystals of azetidine using the manual technique and crystallization was therefore achieved from a sample mounted in a 0.66 mm diameter capillary just held at 170 K, using the laser-assisted zone-refinement technique of Boese & Nussbaumer (1994). Again, the diffraction pattern contained contributions from more than one crystal, but a single crystal could be indexed using the program GEMINI (Bruker, 2003) and integration on the basis of this single component provided good results. In all cases, the exact size of the crystal used for data collection is uncertain, and it is probable that the length along the capillary axis exceeds the size of the X-ray beam.

Table 1

<table>
<thead>
<tr>
<th>Hydrogen-bond geometry (Å, °) for (I).</th>
</tr>
</thead>
<tbody>
<tr>
<td>D—H · · · A</td>
</tr>
<tr>
<td>N5—H5···N1</td>
</tr>
<tr>
<td>N1—H1···N5*</td>
</tr>
</tbody>
</table>

Symmetry code: (i) 1 - x, y + 1/2, z.

Compound (II)

Crystal data

C6H8N

V = 453.41 (7) Å³

Z = 4

Monoclinic, P21/c

Mo Kα radiation

μ = 0.06 mm⁻¹

T = 170 (2) K

0.35 × 0.15 (radius) mm

β = 110.451 (3)°

Data collection

Bruker–Nonius X8 APEXII CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2003)

5429 measured reflections

3.120 (2) reflections

4439 independent reflections

3.102 (2) reflections

760 reflections with I > 2σ(I)

Rint = 0.026

H atoms treated by a mixture of independent and constrained refinement

Δρmax = 0.18 e Å⁻³

Δρmin = −0.17 e Å⁻³

Reference

Bond et al. C6H8N, C6H10N and C6H13N 0545

Figure 7

The unit-cell contents of hexamethyleneimine, showing tetramers linked by co-operative N—H···N hydrogen bonds (dashed lines). The two crystallographically distinct molecules and their symmetry equivalents are distinguished by their shading. H atoms bound to C atoms have been omitted.

organic compounds
Table 2
Hydrogen-bond geometry (Å, °) for (II).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—H1···Ni1</td>
<td>0.84 (2)</td>
<td>2.35 (2)</td>
<td>3.1716 (13)</td>
<td>163.7 (15)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) −x, y − ½, z − z.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N8—H8···Ni1</td>
<td>0.90 (3)</td>
<td>2.27 (3)</td>
<td>3.167 (3)</td>
<td>176 (3)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) 1 − x, 1 − y, −z.

**Refinement**

\[
R[F^2 > 2\sigma(F^2)] = 0.042
\]

\[
wR(F^2) = 0.110
\]

\[
S = 1.06
\]

900 reflections

50 parameters

H atoms treated by a mixture of independent and constrained refinement

Δρ_{max} = 0.16 e Å⁻³

Δρ_{min} = −0.13 e Å⁻³

**Compound (III)**

**Crystal data**

C₆H₁₃N

\[M_r = 99.17\]

Monoclinic, \(P_2_1/n\)

\[a = 11.0201 (14) \text{ Å}\]

\[b = 10.3027 (13) \text{ Å}\]

\[c = 12.7322 (15) \text{ Å}\]

\[\beta = 114.110 (5)°\]

\[V = 1319.5 (3) \text{ Å}^3\]

\[Z = 8\]

Mo \(K\alpha\) radiation

\[\mu = 0.06 \text{ mm}^{-1}\]

\[T = 170 (2) \text{ K}\]

\[\bar{\delta} = 0.35 \times 0.15 (\text{radius}) \text{ mm}\]

16092 measured reflections

2509 independent reflections

1824 reflections with \(I > 2\sigma(I)\)

\[R_{int} = 0.051\]

14 restraints

H atoms bound to C atoms were positioned geometrically and allowed to ride during refinement, with C–H = 0.99 Å and \(U_{eq}(H) = 1.2U_{eq}(C)\). H atoms of the NH groups were located in difference Fourier maps and refined with isotropic displacement parameters. For azetidine and pyrrolidine, no restraints were required. For hexamethyleneimine, the two N–H distances were restrained to a common refined value with standard uncertainty 0.01 Å. Atoms C4, C5, C11 and C12 in hexamethyleneimine were modelled as disordered, each as two components with a site-occupancy factor of 0.5. The C–C bonds in this region (12 in total) were restrained to a common refined value with standard uncertainty 0.01 Å.

Data collection: **SMART** (Bruker, 1997) for (I); **APEX2** (Bruker, 2004) for (II) and (III). For all compounds, cell refinement: **SAINT** (Bruker, 2003); data reduction: **SAINT**. Program(s) used to solve structure: **SIR92** (Altomare et al., 1994) for (I); **SHELXTL** (Sheldrick, 2008) for (II) and (III). For all compounds, program(s) used to refine structure: **SHELXTL**; molecular graphics: **SHELXTL and Mercury** (Macrae et al., 2006); software used to prepare material for publication: **SHELXTL**.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3160). Services for accessing these data are described at the back of the journal.

**References**


