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Azetidine, pyrrolidine and hexamethyleneimine at 170 K

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The crystal structures of the cyclic amines azetidine \((\text{C}_3\text{H}_7\text{N})\), pyrrolidine \((\text{C}_4\text{H}_9\text{N})\) and hexamethyleneimine (homopiperidine, \((\text{C}_6\text{H}_{13}\text{N})\)) of the series \((\text{CH}_2)_n\text{NH}\), 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 \((\text{CH}_2)_n\text{NH}\), for \(n = 2–6\). Azetidine and pyrrolidine contain chains propagating along \(2_1\) screw axes, in which the molecules are linked by co-operative \(\text{N—H}^\cdot\cdot\cdot\text{N}\) 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 \(\text{O—H}^\cdot\cdot\cdot\text{O}\) hydrogen bonds. The next member of the cyclic amine series, heptamethyleneimine, forms a cubic plastic phase on cooling from the melt.

In each structure of the series, molecules are linked by co-operative \(\text{N—H}^\cdot\cdot\cdot\text{N}\) 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 \(2_1\) screw axes in the space group \(P2_1/c\), with one molecule in the asymmetric unit (Fig. 3). In azetidine, the chains also propagate along \(2_1\) screw axes in \(P2_1/c\), but with two crystallographically distinct molecules in each chain (Fig. 4). Thus, every second molecule along the chain is related by the \(2_1\) 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 \(3_1\) 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 \(\text{N—H}^\cdot\cdot\cdot\text{N}\) hydrogen bonds. The rings are formed about crystallographic inversion centres in the space group \(P2_1/n\), with two of the four molecules of the tetramer being crystallographically distinct (Fig. 7).

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 \((\text{CH}_2)_n\text{NH}\), for \(n = 2–6\).
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 hexamethylenimine 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 21 axes, while at high pressure both contain chains along 32 axes (Oswald et al., 2005).
organic compounds

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, with a low barrier for transformation to a postulated lower-symmetry structure in the space group $P\overline{1}$ with four molecules in the asymmetric unit.

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 of the sample, using the manual zone-refinement technique of Boese & Nussbaumer (1994). Again, the diffraction pattern contained contributions from a series of images collected by rotation about the capillary axis, with the capillary remaining in the horizontal position in which the crystal was grown. Moving the capillary away from horizontal at this delicate stage resulted in loss of the crystal, while subsequent cooling (to 170 K) for data collection caused growth of multiple crystals. The orientation matrix established for the initial single crystal was retained and used throughout the data collection and integration, and any possible overlap with diffraction patterns from other crystal components was ignored. For both compounds, this strategy provided acceptable $R_{int}$ values, although the relatively high $R$ values for the refinement of hexamethyleneimine are likely to be attributable largely to more significant overlap in its diffraction pattern. Since there were clearly contributions from many crystals, however, the approximations associated with ignoring overlap completely were preferred to the approximations associated with integration 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 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.

This 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 crystallize the next member of the series, heptamethyleneimine, 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.

![Figure 7](image)

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.

### Compound (I)

**Crystal data**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_r$</td>
<td>57.10</td>
</tr>
<tr>
<td>Monoclinic, $P2_1/c$</td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>9.507 (3) Å</td>
</tr>
<tr>
<td>$b$</td>
<td>9.122 (3) Å</td>
</tr>
<tr>
<td>$c$</td>
<td>9.700 (3) Å</td>
</tr>
<tr>
<td>$\beta$</td>
<td>117.469 (4)$^\circ$</td>
</tr>
<tr>
<td>$V$</td>
<td>573.3 (4) Å$^3$</td>
</tr>
<tr>
<td>$Z$</td>
<td>8</td>
</tr>
<tr>
<td>$\mu$</td>
<td>0.06 mm$^{-1}$</td>
</tr>
<tr>
<td>$T$</td>
<td>170 (2) K</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Mo $K\alpha$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>1.00 × 0.33 (radius) mm</td>
</tr>
</tbody>
</table>

**Data collection**

Bruker SMART APEX CCD area-detector diffractometer

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

4439 measured reflections

1782 independent reflections

1144 reflections with $I > 2\sigma(I)$

$R_{int} = 0.035$

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.162$

$S = 1.04$

1782 reflections

83 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{max} = 0.18$ e Å$^{-3}$

$\Delta\rho_{min} = -0.17$ e Å$^{-3}$

### Table 1

Hydrogen-bond geometry (Å, $^\circ$) for (I).

<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>N5—H5···N1</td>
<td>0.86 (2)</td>
<td>2.27 (2)</td>
<td>3.120 (2)</td>
<td>171.5 (15)</td>
</tr>
<tr>
<td>N1—H1···N5$^a$</td>
<td>0.87 (2)</td>
<td>2.24 (2)</td>
<td>3.102 (2)</td>
<td>174.4 (16)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) $1 - x, y + \frac{1}{2}, -z$.

### Compound (II)

**Crystal data**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_r$</td>
<td>71.12</td>
</tr>
<tr>
<td>Monoclinic, $P2_1/c$</td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>8.6753 (8) Å</td>
</tr>
<tr>
<td>$b$</td>
<td>5.2078 (5) Å</td>
</tr>
<tr>
<td>$c$</td>
<td>10.7108 (10) Å</td>
</tr>
<tr>
<td>$\beta$</td>
<td>110.451 (3)$^\circ$</td>
</tr>
<tr>
<td>$V$</td>
<td>453.41 (7) Å$^3$</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$\mu$</td>
<td>0.06 mm$^{-1}$</td>
</tr>
<tr>
<td>$T$</td>
<td>170 (2) K</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Mo $K\alpha$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>0.35 × 0.15 (radius) mm</td>
</tr>
</tbody>
</table>

**Data collection**

Bruker–Nonius X8 APEXII CCD area-detector diffractometer

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

5429 measured reflections

900 independent reflections

760 reflections with $I > 2\sigma(I)$

$R_{int} = 0.026$
methyleneimine, 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); SHELXLT (Sheldrick, 2008) for (II) and (III). For all compounds, program(s) used to refine structure: SHELXLT: molecular graphics: SHELXL and Mercury (Macrae et al., 2006); software used to prepare material for publication: SHELXLT.

The authors are grateful to the EPSRC (UK), the Danish Natural Science Research Council and the Carlsberg Foundation for funding.

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


**Table 2**

Hydrogen-bond geometry (Å, °) for (II).

<table>
<thead>
<tr>
<th>Bond</th>
<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···N1</td>
<td>0.84 (2)</td>
<td>2.35 (2)</td>
<td>3.1716 (13)</td>
<td>163.7 (15)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry code: (i) −x, y−1, 1−z.

**Table 3**

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

<table>
<thead>
<tr>
<th>Bond</th>
<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···N1</td>
<td>0.90 (2)</td>
<td>2.23 (3)</td>
<td>3.167 (3)</td>
<td>176 (3)</td>
<td></td>
</tr>
<tr>
<td>N1—H1···N1</td>
<td>0.90 (2)</td>
<td>2.25 (3)</td>
<td>3.150 (3)</td>
<td>175 (2)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry code: (i) 1−x, 1−y, z.

**Compound (III)**

**Crystal data**

C4H13N
Mw = 99.17
Monoclinic, P21/c
a = 11.0201 (14) Å
b = 10.3027 (13) Å
c = 12.7322 (15) Å
β = 114.110 (5)°

**Data collection**

Bruker–Nonius X8 APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2003)
Tmin = 0.688, Tmax = 0.981
Refinement

R[F^2 > 2σ(F^2)] = 0.083
wR(F^2) = 0.269
S = 1.12
2509 reflections
173 parameters
14 restraints

H atoms bound to C atoms were positioned geometrically and allowed to ride during refinement, with C—H = 0.99 Å and Uiso(H) = 1.2Ueq(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 hexa-