Crystal Data


Thermal expansion of pyrazine.* By G. De With, Chemical Physics Laboratory, Twente University of Technology, P.O. Box 217, Enschede, The Netherlands

(Received 5 August 1976; accepted 23 August 1976)

The thermal expansion tensor of pyrazine (1,4-diazabenzene, C₄H₄N₂) has been calculated from the changes of the lattice constants with temperature, as measured with X-ray diffraction. The elements of the thermal expansion tensor at 293 K are \( a = -14 \pm 3 \), \( b = 111 \pm 5 \) and \( c = 246 \times 10^{-6} \text{K}^{-1} \).

In order to obtain a more complete picture of the physical data of pyrazine, the thermal expansion tensor was determined. This tensor is relevant for several conversions such as the calculation of isothermal elastic constants from the adiabatic ones and the calculation of \( C_p \) from \( C_v \) (Nye, 1969). From the changes of the crystallographic axes with temperature the thermal expansion tensor can easily be calculated.

A small single crystal was selected from commercially available pyrazine (Merck) and mounted on a Philips PW 1100 computer-controlled diffractometer (Mo K\( \alpha \) radiation, \( \lambda = 0.7107 \text{\AA} \), graphite monochromator, Leyboldt Heraeus NCD1 cooling device). Approximately 80 reflexions, distributed throughout reciprocal space and the \( \theta \) range 4–20°, were accurately centred. This procedure was repeated at five temperatures (Table 1) with the same crystal. At the set points the temperatures were stable within 1 K.

<table>
<thead>
<tr>
<th>Table 1. Lattice constants of pyrazine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Here and in Table 2 (least-squares) standard deviations are given in parentheses and refer to the last significant digit.</td>
</tr>
<tr>
<td>( T (\text{K}) ) &amp; ( a (\text{Å}) ) &amp; ( b (\text{Å}) ) &amp; ( c (\text{Å}) )</td>
</tr>
<tr>
<td>293 &amp; 9.317(1) &amp; 5.911(1) &amp; 3.816(1)</td>
</tr>
<tr>
<td>293* &amp; 9.316(3) &amp; 5.911(3) &amp; 3.815(5)</td>
</tr>
<tr>
<td>252 &amp; 9.321(1) &amp; 5.885(1) &amp; 3.777(1)</td>
</tr>
<tr>
<td>228 &amp; 9.322(1) &amp; 5.873(1) &amp; 3.761(1)</td>
</tr>
<tr>
<td>184† &amp; 9.325(4) &amp; 5.850(2) &amp; 3.733(1)</td>
</tr>
<tr>
<td>18.3 &amp; 9.332(2) &amp; 5.856(1) &amp; 3.731(1)</td>
</tr>
<tr>
<td>132 &amp; 9.330(3) &amp; 5.832(1) &amp; 3.706(1)</td>
</tr>
</tbody>
</table>

* Data taken from Wheatley (1957). The \( b \) and \( c \) axes are interchanged.
† Data taken from de With, Harkema & Feil (1976).

Cell constants were optimized with a least-squares procedure on the Bragg angles of the measured reflexions in two different ways. Firstly, the unit cell was constrained to be orthorhombic according to the accepted space group \( P_{mmm} \) (Wheatley, 1957; de With, Harkema & Feil, 1976). Secondly, no constraints on the unit-cell angles were applied. No essential differences between these two refinements were found. The unit-cell angles remained at 90° within experimental error. This is another confirmation of Neumann’s principle (Nye, 1969). The results of the orthorhombic refinements are given in Table 1. For comparison the cell constants as given by Wheatley (1957) and de With, Harkema & Feil (1976) are included in Table 1. In view of the fact that pyrazine crystals are highly deformable, the comparison is good.

The measured data have been least-squares fitted by a two-term polynomial in \( T \) (Table 2).

<table>
<thead>
<tr>
<th>Table 2. Fit to the measured data</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = k_0 + k_2 T^2 ) where ( x ) denote either ( a, b ) or ( c ).</td>
</tr>
<tr>
<td>( x ) &amp; ( k_0 ) &amp; ( k_2 \times 10^4 ) &amp; ( \rho )</td>
</tr>
<tr>
<td>( a ) &amp; 9.336(2) &amp; -0.22(5) &amp; 0.933</td>
</tr>
<tr>
<td>( b ) &amp; 5.815(3) &amp; 1.12(5) &amp; 0.977</td>
</tr>
<tr>
<td>( c ) &amp; 3.677(1) &amp; 1.60(2) &amp; 0.999</td>
</tr>
</tbody>
</table>

\( \rho \) is the correlation coefficient between measured and calculated unit-cell axes.

It was suggested by Momany, Carruthers, McGuire & Scheraga (1974) from crystal packing considerations, that upon contraction of the \( c \) axis the \( a \) axis should expand. This suggestion has now been verified.

* This research has been carried out under the auspices of the Foundation for Fundamental Research on Matter by Electron and X-rays (FOMRE) and with aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

References


