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The Crystal Structure of Imidazole at 103 K by Neutron Diffraction

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Abstract

At 103 K, imidazole, $C_3H_4N_2$, is monoclinic, space group $P2_1/c$, with four molecules per unit cell and has lattice parameters $a = 7.569$ (1), $b = 5.366$ (1), $c = 9.785$ (2) Å, and $\beta = 119.08$ (1)°. The neutron structure determination using 1095 reflections gave $R(F^2) = 0.026$ and $R_w(F^2) = 0.041$. The e.s.d.'s in bond lengths (0.001 Å for C–C, C–N) and angles are smaller than in previous X-ray and neutron determinations of this structure. The improved precision was needed in connection with an X-ray study of the charge density of imidazole.

Introduction

Neutron structure determinations of imidazole (Fig. 1) at 293 K and 123 K have been reported by Craven, McMullan, Bell & Freeman (1977), hereafter CMBF. In a subsequent low-temperature X-ray determination by Epstein, Ruble & Craven (1978), hereafter ERC, the crystal was cooled in a stream of nitrogen gas at a recorded temperature of 123 K. However, it was noted (Table 1) that there were significant differences in the

X-ray cell parameters from the 123 K values of Martinez-Carrera (1966). Also, in least-squares refinements of the structure using reflections with $\sin \theta/\lambda > 1.0$ Å^{-1}, the carbon and nitrogen X-ray U_{ij} values were found to be substantially different from the corresponding CMBF neutron values. These differences
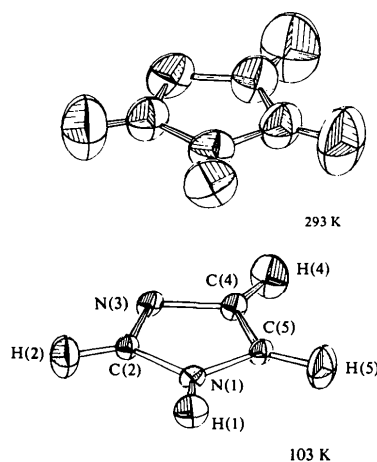

Fig. 1. Atomic nomenclature for imidazole and 50% probability ellipsoids (Johnson, 1976).

Table 1. *Crystal data for imidazole*

Monoclinic, $P2_1/c$; $Z = 4(C_3H_4N_2)$/unit cell.

| | Neutron diffraction measurements | | | | | X-ray diffraction measurements | |
	103 K[1]	108 K[1]	113 K[1]	123 K[1]	293 K[4]	ERC[2]	123 K[3]
a	7·569 (1) Å	7·572 (2) Å	7·577 (2) Å	7·583 (1) Å	7·732 (4) Å	7·567 (1) Å	7·582 (2) Å
b	5·366 (1)	5·368 (1)	5·373 (1)	5·375 (1)	5·458 (2)	5·371 (1)	5·371 (2)
c	9·785 (2)	9·782 (2)	9·777 (3)	9·779 (2)	9·779 (4)	9·781 (2)	9·790 (3)
β	119·08 (1)°	119·03 (1)°	118·93 (2)°	118·92 (1)°	117·26 (3)°	119·05 (1)°	118·98 (2)°
λ	1·0508 (1) Å	1·0508 (1) Å	1·0508 (1) Å	1·0508 (1) Å	1·1690 (4) Å	0·7093 Å	1·5418 Å
						(Mo $K\alpha_1$)	(Cu $K\alpha$)

(1) This study. (2) Epstein, Ruble & Craven (1978). (3) Martínez-Carrera (1966). (4) Craven, McMullan, Bell & Freeman (1977).

were greater than those which sometimes occur when neutron and X-ray data are collected at the same temperature. Thus, systematic differences (ΔU_{ij}, ~10σ) are reported for parabanic acid at room temperature (Craven & McMullan, 1979), which some might attribute to the effects of thermal diffuse scattering.

It was suspected that the neutron (CMBF) and the X-ray (ERC) data corresponded to significantly different temperatures. This gave concern that systematic errors would arise in the low-temperature charge density analysis by assuming the CMBF neutron values for either positional or thermal atomic parameters.

An additional neutron structure determination at 103 ($\pm$1) K, which is presently reported, has given more precise atomic parameters than in either of the previous determinations by CMBF. From comparisons with new neutron cell data measured at four temperatures, it is estimated that the X-ray data of ERC were measured at 108 $\pm$ 5 K rather than the recorded temperature of 123 K. Values for the new neutron thermal parameters appear to be consistent with the 293 K values of CMBF (Fig. 1), but there are unreconciled differences from the 123 K values of CMBF.

Experimental

Imidazole was crystallized by slow cooling of a saturated benzene solution (308 to 298 K). The crystals were prisms with [001] elongation, exhibiting the forms {100}, {110} and {001}. The crystal used for neutron diffraction measured (1·4 × 1·7 × 3·9 mm) and had a volume of 8·6 mm³. It was a fragment cut from an elongated crystal and shaped by grinding to give an artificial (001) face.

The neutron data were collected with a four-circle automated diffractometer on the High Flux Beam Reactor of the Brookhaven National Laboratory using a monochromated beam obtained by reflection from the (002) plane of a beryllium crystal. The neutron wavelength of 1·0508 (1) Å was determined by measurement of the lattice parameter ($a_0 = 6·5964$ Å) of a standard KBr crystal at room temperature.

The imidazole crystal was glued onto a hollow aluminum pin and sealed under a quartz dome. The assembly was cooled and maintained at constant temperature ($\pm$1 K) inside a closed-cycle helium refrigerator† constructed of aluminum which was mounted within the diffractometer χ-circle. The crystal c^* axis was within a few degrees of the diffractometer φ axis.

Imidazole lattice parameters were determined by a least-squares fit to the neutron diffractometer $\sin^2 \theta$ values for 28 reflections with $38° < 2\theta < 60°$. The temperature for the neutron data collection was selected by minimizing $D = \sum (\Delta/\sigma)^2$ as a function of temperature. In this expression, the sum is with respect to the cell parameters a,b,c, $\cos \beta$ where Δ is the observed difference between corresponding neutron and X-ray values, and σ is the e.s.d. in Δ. For neutron cell data at 123, 113 and 103 K, comparison with the X-ray cell data of Epstein, Ruble & Craven (1978) (Table 1) gave $D = 154$, 31 and 13 respectively. Because of time limitations it was then decided to proceed with the neutron data collection at 103 K. Afterwards, there was time for the cell data to be measured at 108 K (Table 1), which gave $D = 7$. Although it would have been preferable to collect neutron data at 108 K, it is estimated from the D values that the crystal temperatures for the neutron and X-ray data have been matched within about 5 K. The neutron cell data at 123 K are in reasonable agreement with the corresponding X-ray cell data (Martínez-Carrera, 1966), giving $D = 18$.

The neutron integrated intensities were measured using $\omega/2\theta$ step scans with an incident beam monitor registering a preset count at each step. Scan widths were 3° in 2θ for reflections with $\sin \theta/\lambda \leq 0·40$ Å⁻¹ and were varied according to the dispersion formula $\Delta(2\theta) = 3·5 + 1·7 \tan \theta$ for reflections with $0·40$ Å⁻¹ < $\sin \theta/\lambda < 0·76$ Å⁻¹. The neutron scattering from the cryostat and quartz surrounding the crystal was examined by scanning over the entire 2θ range at $\chi = 0$, 45 and 90°. The φ angles were chosen to avoid Bragg diffraction from the imidazole crystal. The features in

† Air Products and Chemicals, Inc. DISPLEX® Model CS-202.

these scans were broad and it was therefore considered unnecessary to take them into account in estimating backgrounds. The integrated intensity (I) for each reflection was obtained by subtracting the background (B) evaluated from the first and last tenth of the total scan. The variance in an intensity was assumed to be $\sigma^2(I) = I + 5B + (0.02I)^2$. Neutron absorption corrections were applied using an analytical procedure (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973). The linear absorption coefficient ($\mu = 0.176$ mm^{-1}) was calculated assuming the mass absorption coefficient for chemically bonded hydrogen to be 23.9 m^3 Mg^{-1} (McMullan, Fox & Craven, 1978). The resulting crystal transmission factors were found to range between 0.68 and 0.81.

Intensities were measured for 1159 reflections in a quadrant of reciprocal space, including 64 pairs of reflections measured as both $hk0$ and $\bar{h}k0$. Average

Table 2. Atomic positional parameters and their e.s.d.'s

Fractional coordinates are given for non-hydrogen atoms ($\times 10^5$) and for hydrogen ($\times 10^4$).

	x	y	z
N(1)	21891 (5)	33257 (6)	8710 (4)
C(2)	15699 (7)	21884 (9)	17916 (6)
N(3)	20840 (5)	34584 (7)	30898 (4)
C(4)	30927 (8)	55227 (10)	29901 (6)
C(5)	31694 (8)	54606 (10)	16221 (6)
H(1)	2034 (2)	2671 (2)	−188 (1)
H(2)	767 (2)	443 (2)	1503 (2)
H(4)	3706 (3)	6913 (3)	3898 (2)
H(5)	3843 (2)	6723 (3)	1150 (2)

values were assumed for the latter, giving an agreement factor $\sum |\langle F^2 \rangle - F^2|/\sum \langle F^2 \rangle = 0.008$ for the zone. Of the 1095 reflections, there were 29 with insignificantly negative intensities.

Full-matrix least-squares refinement was carried out with a modified version of the computer program by Busing, Martin & Levy (1962), so as to minimize $\sum w\Delta^2$ where $\Delta = (F_{obs})^2 - (F_{calc})^2$ and $w = 1/\sigma^2(F_{obs}^2)$. Neutron scattering lengths ($\times 10^{-11}$ mm) were assumed to be 0.6648 for carbon, 0.940 for nitrogen and -0.374 for hydrogen (Shull, 1972). The initial values of the structure parameters were those reported by CMBF for 123 K. An isotropic extinction parameter was included, assuming that extinction was of type I with a Lorentzian distribution of crystal mosaicity (Becker & Coppens, 1974). In the final refinement cycle, all parameter changes were less than 0.01σ. The agreement factors were then $R = (\sum \Delta)/(\sum F^2) = 0.026$, $R_w = [(\sum w\Delta^2)/(\sum wF^4)]^{1/2} = 0.041$ and $[\sum w\Delta^2/(n_{obs} - n_{param})]^{1/2} = 1.28$. In contrast to the previous low-temperature neutron determination by CMBF, there was significant neutron extinction with $g = 0.097$ (5) $\times 10^4$. The most severe correction ($0.74F_{calc}^2$) was for the reflection 200, and there were seven other reflections with correction factors less than 0.90. The final nuclear positional parameters with e.s.d.'s are in Table 2.*

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* Tables of anisotropic thermal parameters and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34083 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths and angles at 103 K

	Uncorrected*	Corrected†		Uncorrected*	Corrected†
N(1)—C(2)	1.347 Å	1.358 Å	C(5)—N(1)—C(2)	107.1°	107.2°
N(1)—C(5)	1.369	1.381	N(1)—C(2)—N(3)	111.9	111.8
C(2)—N(3)	1.323	1.333	C(2)—N(3)—C(4)	105.1	105.3
N(3)—C(4)	1.375	1.389	N(3)—C(4)—C(5)	109.8	109.8
C(4)—C(5)	1.368	1.378	C(4)—C(5)—N(1)	106.0	106.0
N(1)—H(1)	1.045	1.053	C(5)—N(1)—H(1)	125.7	125.7
C(2)—H(2)	1.077	1.087	C(2)—N(1)—H(1)	127.1	127.0
C(4)—H(4)	1.077	1.086	N(1)—C(2)—H(2)	123.7	123.7
C(5)—H(5)	1.077	1.087	N(3)—C(2)—H(2)	124.4	124.5
			N(3)—C(4)—H(4)	122.1	122.2
Non-bonded close interactions			C(5)—C(4)—H(4)	128.1	128.0
H(1)···H(2)	2.508		C(4)—C(5)—H(5)	131.1	131.1
H(2)···N(3)	2.605		N(1)—C(5)—H(5)	122.8	123.0
H(4)···H(5)	2.276				
Hydrogen bond					
N(1)···N(3)	2.849		N(1)—H(1)···N(3)	173.3	
H(1)···N(3)	1.809				

* Bond lengths between non-hydrogen atoms have standard deviations of 0.001 Å and those to hydrogen have standard deviations of 0.002 Å. The standard deviations in bond angles are $0.05°$ for angles not involving hydrogen and $0.1°$ for angles involving hydrogen.

† Values are corrected for rigid-body librations assuming the librational tensor from Table 4.

Discussion

Bond lengths and angles for imidazole (Table 3) have been determined with greater precision than the previously reported neutron values (CMBF). Uncorrected bond lengths at 103 K are slightly longer than at 293 K, the most significant difference (0·011 Å with e.s.d. 0·002 Å) being in the bond C(4)—C(5). This effect is attributed to the smaller anisotropic thermal vibrations at low temperature (Fig. 1). Just as for the values at 293 K, the observed thermal parameters at 103 K gave good agreement (Table 4) with those of a rigid body (Schomaker & Trueblood, 1968). There was improved agreement between the bond lengths and angles at 103 and 293 K after corrections for rigid-body libration were made (Table 3). However, the 293 K values become marginally longer with the most significant difference (0·011 Å with e.s.d. of 0·004 Å) being in the bond C(2)—H(2). The corrections at 293 K might be slightly overestimated.

Table 4. *Rigid-body analysis for imidazole thermal motion*

(1) Tensor components referred to crystal axes a,b,c^*

Translational tensor, T ($Å^2 \times 10^4$)	111 (12)	36 (10)	15 (10)
		144 (10)	25 (9)
			47 (10)
Librational tensor, L [$(°)^2$]	26 (2)	4 (1)	−11 (1)
		25 (3)	4 (2)
			41 (2)
Cross tensor, S[$Å(°) \times 10^2$]	4 (4)	−4 (2)	5 (2)
	8 (3)	−1 (5)	3 (3)
	−7 (2)	2 (3)	−3 (3)

(2) RMS value of the differences $(U_{ij})_{obs} - (U_{ij})_{calc}$ referred to axes a,b,c^* is 0·0018 $Å^2$.

(3) Principal axes of L and the angles which they make with the molecular axes of inertia (I_x,I_y,I_z), as shown in Fig. 2 of CMBF.

		I_x	I_y	I_z
L_1	17·1 $(°)^2$	91·0°	92·8°	3·0°
L_2	28·1	3·5	86·9	88·4
L_3	46·8	87·1	176·0	92·8

Table 5. *Best molecular least-squares plane*

(1) The equation of the plane with respect to the crystallographic axes

$$5·5539x - 2·6929y + 0·4267z = 0·3583,$$

where the coefficients are in Å; and x,y,z are fractional coordinates.

(2) Displacements of atoms from the plane.

(a) Atoms in the plane		(b) Other atoms	
N(1)	−0·001 (1) Å	H(1)	0·044 Å
C(2)	0·001 (1)	H(2)	0·013
N(3)	0·000 (1)	H(4)	0·005
C(4)	0·000 (1)	H(5)	0·015
C(5)	0·001 (1)		

The ring atoms are coplanar (Table 5). The hydrogen atoms are all displaced towards the same side of this plane, as previously reported. The only difference is that H(4) has a smaller displacement (0·005 Å at 103 K; 0·020 Å at 293 K). This may arise from an intramolecular anharmonic vibration of H(4), which is damped at the lower temperature.

The thermal ellipsoids for the molecule at 293 and 103 K (Fig. 1) have similar orientations for corresponding atoms, with the greatest differences being for the atoms N(1), H(1) of the hydrogen-bonding donor group. All the thermal ellipsoids shown for the lower temperature in Fig. 1 of CMBF are considerably different in orientation from those in the present Fig. 1 and are closer in size to those at 293 rather than 103 K. The substantial differences between U_{ij} values at the lower temperatures are attributed in part to unidentified systematic errors. It should be noted that the low-temperature CMBF neutron intensity data were collected with different experimental facilities and procedures from those described here. Lattice parameters were not measured during the neutron data collection at 123 K (CMBF) in order to provide an independent check on the temperature. It is suspected that the crystal was warmer than indicated by the thermocouple measurement.

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