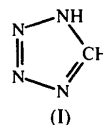


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$\beta = 116.69(3)^\circ$ and space group $P2_1$ or $P2_1/m$. Unfortunately, the diffraction data were of rather poor quality and the R value was 0.11. As we were interested in obtaining an accurate structure of tetrazole as part of an investigation into the packing and intermolecular hydrogen bonding in N-containing five-membered ring systems, we decided to reinvestigate the crystal structure. Crystals were grown from *n*-pentane by the convection method described by Arend, Huber, Freudenreich & Surbeck (1979), and we were surprised to discover that we had obtained the triclinic form of tetrazole. We report here the crystal structure of α -tetrazole, (I), and compare it with its monoclinic polymorph.



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α -1H-1,2,3,4-Tetrazole

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Abstract

A polar polymorph of tetrazole is described. α -Tetrazole, CH_2N_4 , is triclinic (space group $P1$), with one molecule of the 1H-tautomeric form of tetrazole in the unit cell. The molecules are connected by N—H...N hydrogen bonds forming chains, which are linked together by C—H...N interactions to give planar sheets separated by 3.35 (1) Å. The structure of α -tetrazole is compared with that of monoclinic β -tetrazole; the difference in the two structures is due to the sheet orientation.

Comment

McCrone, Grabar & Lieber (1957) reported the crystallographic data of tetrazole crystals derived from crystal morphology measurements and X-ray diffraction data. They concluded that tetrazole crystallizes in a triclinic unit cell of dimensions $a = 5.00$, $b = 5.46$, $c = 3.75$ Å, $\alpha = 130$, $\beta = 111$ and $\gamma = 63^\circ$, but the crystal structure was not determined. We shall call this form α -tetrazole. Later, van der Putten, Heijdenrijk & Schenk (1974) determined the crystal structure of a monoclinic form of tetrazole, which we shall call here β -tetrazole. This structure contains two molecules in a unit cell of dimensions $a = 4.931(2)$, $b = 6.451(2)$, $c = 5.390(1)$ Å,

Bond distances within the ring differ significantly, with the shortest bond between the N2 and N3 atoms [1.295 (3) Å], consistent with the formulation of a formal double bond between these atoms. The neighbouring N3—N4 bond of 1.346 (3) Å is the longest in the ring, suggesting there is considerable localization of charge within the ring. The N1—C5 bond is slightly shorter than the C5—N4 distance, although the formal double bond lies between the latter atoms. The N1—H1 and C5—H5 distances at 0.81 (5) and 0.88 (4) Å, respectively, are artificially short, as expected, but the bond angles around the N1 and C5 atoms are sensible, indicating that the angles associated with the H atoms are reliable.

Except for N4—C5, bond distances within the ring are consistently shorter than those observed at 150 K for 1-methyltetrazole (Palmer & Parsons, 1996) (see Table 3). This is mostly due to libration effects, as shown by TLS-corrected values (Schomaker & Trueblood, 1968), though the TLS R factors are fairly high at 17% for this structure and 18% for the methyl analogue. Bond angles are similar for the two structures.

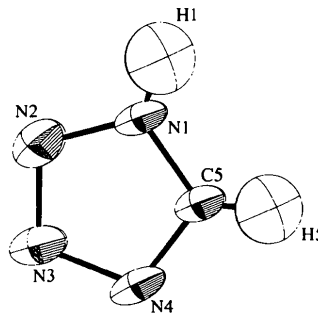


Fig. 1. View of the title molecule showing the atomic labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

Inspection of the packing of the molecules (Fig. 2) reveals that the individual molecules are linked by N—H...N bridges forming chains, which are in turn connected by C—H...N bridges to form a two-dimensional network or sheet. The intermolecular N—H...N distance at 2.804 (2) Å [N1—H1...N4(*x*, *y*, 1 + *z*)] is short and represents by far the strongest intermolecular interaction. The molecules making up each sheet are almost coplanar (r.m.s. deviation of atoms from the mean plane is 0.06 Å). The reason for this is unclear. Certainly, each molecule in the sheet is surrounded by six neighbours consistent with close-packing of molecules (total number of nearest neighbours is 12), but this is not a prerequisite of coplanarity. A more likely cause is a bifurcated C—H...N bonding interaction between adjacent molecules [3.308 (3) Å for C5—H5...N2(*x* - 1, *y* - 1, *z* - 1) and 3.377 (3) Å for C5—H5...N3(*x* - 1, *y* - 1, *z*)] (see Fig. 2). The distance between the sheets is 3.35 (1) Å, which is the same as the interplanar distance in graphite. Since all the molecules are parallel, the packing can be considered as graphitic. Interestingly, this heteroaromatic system does not fit into one of the packing schemes described by Desiraju & Gavezzotti (1989) for polynuclear aromatic hydrocarbons.

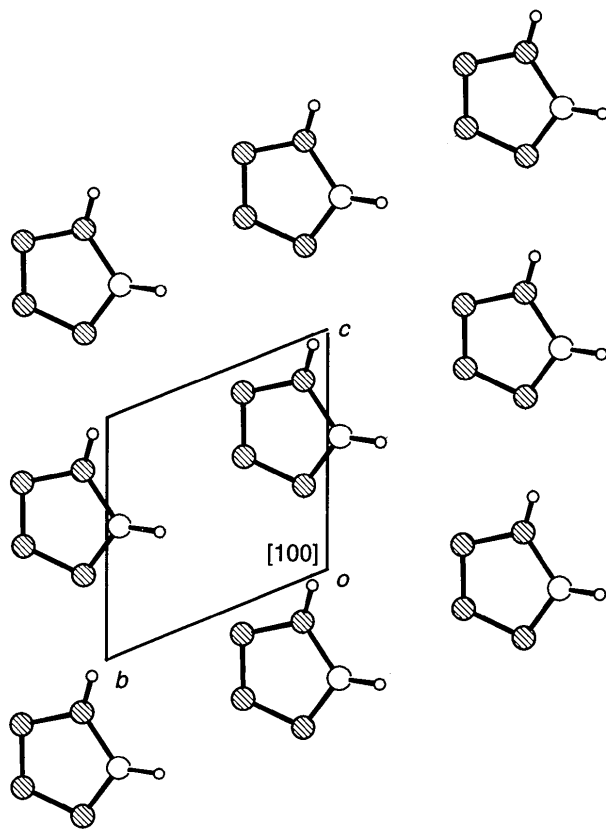


Fig. 2. The unit cell of α -tetrazole, viewed along *a* from the origin, showing the N—H...N and C—H...N bonding interactions (N atoms shaded).

In view of the large errors associated with determination of the structure of β -tetrazole (van der Putten *et al.*, 1974), it is not worthwhile comparing the geometry of the tetrazole molecules obtained in the two studies. It is, however, instructive to compare the arrangement of the molecules in the respective unit cells. In β -tetrazole, the molecules are also arranged in parallel sheets (sheet separation 3.23 Å, half the unit cell *b* axis length). Indeed, the arrangement of the molecules in the sheets is similar for both structures, but whereas in β -tetrazole the molecules in alternate sheets point in different directions (dipole moments cancel), in α -tetrazole all molecules point in the same direction (dipole moments additive), in spite of the large molecular dipole moments (Krugh & Gold, 1974).

In order to establish that this triclinic form of tetrazole was indeed identical with that reported by McCrone *et al.* (1957), we simulated a powder diffraction pattern using the single-crystal intensity data and the associated lattice parameters (Bartsch & Goddard, 1996). There was a good agreement between the *d* values and *III*, intensities for all the principal lines. We were able to transform our unit cell to one closely resembling that reported by McCrone *et al.* and obtained the following unit cell constants: *a* = 4.936, *b* = 5.434, *c* = 3.725 Å, α = 120.6, β = 107.2 and γ = 62.6°. Only the α angle differed significantly (120.6 *versus* 130°) from that reported.

The calculated densities of the two crystal forms are almost the same (α -tetrazole 1.53 and β -tetrazole 1.52 Mg m⁻³). Similarly, the packing coefficient of α -tetrazole at 0.7233 is only slightly smaller than that for β -tetrazole (0.7379), indicating that both structures are close-packed (Kitaigorodsky, 1973). (Packing coefficients were calculated using the following van der Waals radii: C 1.80, H 1.17, N 1.58 Å; molecular volumes were calculated at a resolution of 0.02 Å; for details of the program used see Goddard, Haenel, Herndon, Krüger & Zander, 1995). A differential scanning calorimetry measurement of the crystals gave no indication of a phase transition between the two polymorphs, only a broad melting peak at 438 K. Although the arrangement of the tetrazole molecules in the layers is the same in the two crystal forms and the sheets can thus be considered as synthons in crystal engineering (Desiraju, 1995), the fact that at least two crystal polymorphs occur in this case illustrates the difficulty of using them to predict crystal structures (Gavezzotti, 1994).

Experimental

Crystals of the title compound were grown by the convection method from *n*-pentane (Arend *et al.*, 1979). The warmest part of the apparatus was maintained at 299 K and the coolest part 294 K. Crystals suitable for data collection were obtained after about three weeks. The colourless prisms exhibited good extinction under a polarizing microscope and the crystal

chosen for study showed narrow unsplit peaks from ω scans of several selected low-angle reflections in various directions. Other crystal samples grown by sublimation or by cooling a saturated solution were not found to be satisfactory for diffraction experiments.

Crystal data

CH ₂ N ₄	Mo K α radiation
$M_r = 70.07$	$\lambda = 0.71069 \text{ \AA}$
Triclinic	Cell parameters from 25 reflections
$P1$	$\theta = 2-26.3^\circ$
$a = 3.725 (1) \text{ \AA}$	$\mu = 0.120 \text{ mm}^{-1}$
$b = 4.773 (1) \text{ \AA}$	$T = 293 \text{ K}$
$c = 4.936 (1) \text{ \AA}$	Prism
$\alpha = 107.03 (2)^\circ$	$0.30 \times 0.18 \times 0.17 \text{ mm}$
$\beta = 107.23 (2)^\circ$	Colourless
$\gamma = 101.57 (2)^\circ$	
$V = 76.09 (3) \text{ \AA}^3$	
$Z = 1$	
$D_x = 1.529 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.01$
$\omega-2\theta$ scans	$\theta_{\text{max}} = 27.4^\circ$
Absorption correction: none	$h = -4 \rightarrow 4$
774 measured reflections	$k = -6 \rightarrow 6$
690 independent reflections	$l = -6 \rightarrow 6$
661 reflections with $I > 2\sigma(I)$	3 standard reflections
	frequency: 30 min
	intensity decay: none

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
$R(F) = 0.042$	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
$wR(F^2) = 0.099$	Extinction correction: none
$S = 1.12$	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
690 reflections	Absolute configuration: Flack (1983)
54 parameters	Flack parameter = $-1 (4)$
H atoms refined freely	
$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} < 0.001$	

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

U_{iso} for H atoms, $U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \cdot a_i \cdot a_j$ for C and N atoms.				
	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
C5	-0.0210 (5)	-0.0582 (4)	0.5320 (4)	0.0432 (4)
N1	0.1301 (4)	0.1086 (3)	0.8255 (3)	0.0445 (4)
N2	0.3687 (5)	0.3823 (4)	0.8753 (4)	0.0561 (5)
N3	0.3573 (5)	0.3769 (4)	0.6090 (4)	0.0546 (5)
N4	0.1155 (4)	0.1037 (4)	0.3888 (4)	0.0475 (4)
H1	0.078 (9)	0.064 (9)	0.958 (10)	0.082 (10)
H5	-0.199 (10)	-0.241 (10)	0.439 (10)	0.077 (10)

Table 2. Selected geometric parameters (\AA , $^\circ$)

C5—N1	1.308 (2)	N1—H1	0.81 (5)
C5—N4	1.315 (2)	N2—N3	1.295 (3)
C5—H5	0.88 (4)	N3—N4	1.346 (3)
N1—N2	1.332 (2)		

N1—C5—N4	108.8 (2)	N2—N1—H1	123 (3)
N1—C5—H5	127 (3)	N3—N2—N1	106.0 (2)
N4—C5—H5	124 (3)	N2—N3—N4	110.5 (2)
C5—N1—N2	109.2 (2)	C5—N4—N3	105.5 (2)
C5—N1—H1	127 (3)		

Table 3. Bond lengths (observed and TLS corrected, \AA) in α -tetrazole and 1-methyltetrazole

	α -Tetrazole obs/corr	1-Methyltetrazole obs/corr
N1—N2	1.332 (2)/1.347	1.344 (2)/1.346
N2—N3	1.295 (3)/1.311	1.299 (2)/1.303
N3—N4	1.346 (3)/1.365	1.360 (2)/1.362
N4—C5	1.315 (2)/1.329	1.315 (2)/1.318
C5—N1	1.308 (2)/1.327	1.331 (2)/1.335

The combination of cell constants and wavelength does not permit a reliable determination of the absolute structure.

Data collection: *CAD-4 Express Software* (Enraf-Nonius, 1994). Cell refinement: *CAD-4 Express Software*. Data reduction: *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1151). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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