

ω oscillation 0.30°;
30 s/frame
Absorption correction: none
15 404 measured reflections
3064 independent reflections

$R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 26.39^\circ$
 $h = -10 \rightarrow 10$
 $k = -19 \rightarrow 19$
 $l = -14 \rightarrow 14$
Intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.127$
 $S = 1.053$
3064 reflections
196 parameters
H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.3262P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.14 \text{ e } \text{Å}^{-3}$
Extinction correction:
SHELXL97 (Sheldrick, 1997)
Extinction coefficient:
0.0103 (16)
Scattering factors from
International Tables for Crystallography (Vol. C)

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Table 1. Selected geometric parameters (Å, °)

C1—C7	1.463 (2)	C8—C11	1.468 (2)
C7—C8	1.324 (2)		
O2—C3—C4	126.9 (1)	C7—C8—C11	125.6 (2)
C8—C7—C1	128.7 (2)	O3—C13—C12	124.9 (1)
C6—C1—C7—C8	-5.1 (3)	C7—C8—C11—C12	-3.4 (3)
C1—C7—C8—C11	-178.3 (2)		

Data collection: *SMART* (Siemens, 1994a). Cell refinement: *SAINTE* (Siemens, 1994a). Data reduction: *SAINTE* and *XPREP* (Siemens, 1996). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994b). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1301). Services for accessing these data are described at the back of the journal.

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5-Methyl-1H-tetrazole

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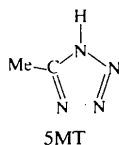
Abstract

We have determined the molecular structure of the title compound, C₂H₄N₄, using X-ray crystallography. The tetrazole ring is expected to be an aromatic system. The ring structure is not very different from that of 1-methyltetrazole. The C—C bond length is shorter than expected and this indicates that the electron of the tetrazole ring expands to the methyl group.

Comment

As part of a study of the aromaticity of tetrazole rings, we are interested in the effects of substituents on the ring structure. Some crystal structures of tetrazole derivatives have been reported previously. The parent compound, 1H-tetrazole (1HT), was reported by Goddard *et al.* (1997). The compound substituted with a methyl group at the 1-position, 1-methyltetrazole (1MT), was reported by Palmer & Parsons (1996). However, the structure of 5-methyl-1H-tetrazole (5MT), which is substituted at the 5-position by a methyl group, has not been previously reported. We therefore determined the crystal structure of the title compound using X-ray crystallography, and compared it with the earlier compounds. It has also been reported that 1HT and 1MT have almost the same

thermal stability, while 5MT is more thermally stable than either of them (Wu *et al.*, 1994). We therefore investigated the effect of the substituent position on thermal stability.



The tetrazole ring in 5MT is almost planar. The N—N and C—N single bond lengths are shorter than the expected values and the N=N and C=N double bond lengths are longer. This indicates resonance effects and this result is the same as has been found for the other tetrazoles, for example, 1HT (Goddard *et al.*, 1997), 1MT (Palmer & Persons, 1996) and 1-phenyltetrazole (Matsunaga *et al.*, 1999). With regard to intermolecular interactions, the N1—H1...N4 distance of 2.811 (3) Å [N1—H1...N4(*x*, 1 - *y*, *z* - ½)] is short and this indicates a strong interaction. This is the same as in 1HT.

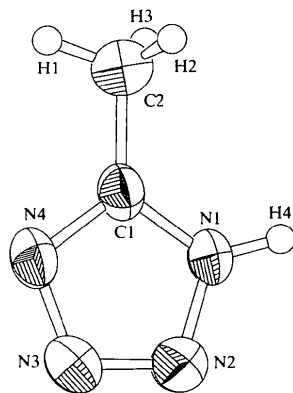


Fig. 1. View of the title molecule with the atomic numbering scheme and with non-H atoms represented by 50% probability ellipsoids. H atoms are shown as spheres of an arbitrary radius.

Compared with 1HT, the N—N and C—N single bond lengths in 5MT are longer and the C=N and N=N bond lengths are shorter or equal. In particular, the C1—N1 bond is much longer in 5MT. This indicates that 5MT is more localized than 1HT.

The bond lengths of the tetrazole ring in 5MT are not very different from those in 1MT; only the N2=N3 bond length is slightly different, being 1.285 (3) in 5MT and 1.299 (2) Å in 1MT. The C1—C2 bond length of 1.473 (3) Å in 5MT is slightly shorter than in comparable compounds. For example, the C—C bond lengths of *p*-nitrotoluene (Barve & Pant, 1971) and *p*-xylene (Koningsveld *et al.*, 1986) are 1.528 and 1.503 (2) Å, respectively. This indicates that the electron

of the tetrazole ring in 5MT expands to the methyl group. On the other hand, the N1—C bond length [1.455 (2) Å] in 1MT does not differ from normal N—C bond lengths; for example, that of 1-methylthymine is 1.460 (3) Å (Frey *et al.*, 1973). This indicates that the methyl group at the 1-position has less influence on the delocalization than when at the 5-position. This could be one of the reasons why 5MT is more thermally stable than 1MT.

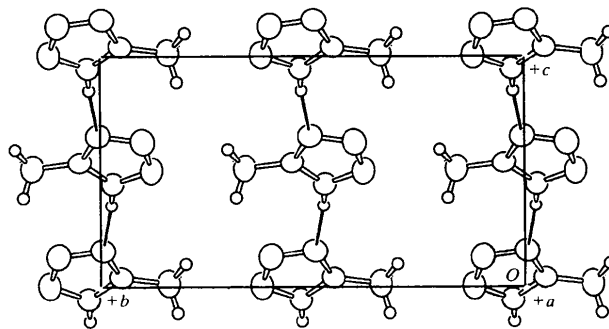


Fig. 2. Packing diagram of 5MT, with the hydrogen bonds illustrated by solid lines.

Experimental

Crystals of the title compound were obtained by recrystallization from ethyl acetate.

Crystal data

C₂H₄N₄
M_r = 84.08
 Monoclinic
Cc
a = 4.586 (2) Å
b = 12.843 (4) Å
c = 9.767 (1) Å
 β = 133.98 (2)°
V = 413.9 (3) Å³
Z = 4
D_x = 1.349 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 16 reflections
 θ = 8.6–12.6°
 μ = 0.101 mm⁻¹
T = 296.2 K
 Plate
 0.70 × 0.60 × 0.05 mm
 Colourless

Data collection

MacScience MXC 18 diffractometer
 ω scans
 Absorption correction: none
 1025 measured reflections
 950 independent reflections
 768 reflections with $I > 2\sigma(I)$

R_{int} = 0.019
 θ_{\max} = 27.5°
h = -5 → 5
k = -16 → 16
l = -5 → 12
 3 standard reflections every 100 reflections
 intensity decay: 10%

Refinement

Refinement on *F*
R = 0.040
 wR = 0.052

$w = 1/[\sigma^2(F_o) + 0.00048|F_o|^2]$
 $(\Delta/\sigma)_{\max} = 0.043$

$S = 1.859$
 768 reflections
 53 parameters
 H-atom parameters not refined

$\Delta\rho_{\max} = 0.10 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
N1	0.4964	0.5289 (1)	-0.0532	0.0453 (5)
N2	0.4712 (8)	0.6205 (1)	0.0040 (4)	0.0600 (6)
N3	0.4630 (8)	0.5991 (2)	0.1298 (4)	0.0613 (6)
N4	0.4815 (7)	0.4946 (2)	0.1559 (4)	0.0511 (5)
C1	0.5011 (8)	0.4519 (2)	0.0399 (4)	0.0425 (5)
C2	0.525 (1)	0.3401 (2)	0.0148 (5)	0.0662 (7)

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

N1—N2	1.342 (3)	N3—N4	1.358 (3)
N1—C1	1.333 (2)	N4—C1	1.316 (3)
N2—N3	1.285 (3)	C1—C2	1.473 (3)
N2—N1—C1	109.4 (2)	N1—C1—N4	107.4 (2)
N1—N2—N3	106.2 (2)	N1—C1—C2	125.2 (2)
N2—N3—N4	110.6 (2)	N4—C1—C2	127.4 (2)
N3—N4—C1	106.5 (2)		
N1—N2—N3—N4	-0.1 (2)	N2—N3—N4—C1	-0.1 (3)
N1—C1—N4—N3	0.3 (2)	N3—N2—N1—C1	0.3 (2)
N2—N1—C1—N4	-0.4 (2)	N3—N4—C1—C2	-179.9 (2)
N2—N1—C1—C2	179.8 (2)		

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

<i>D</i> — <i>H</i> ... <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> — <i>H</i> ... <i>A</i>
N1—H4...N4 ⁱ	0.87	1.94	2.811 (3)	173.4

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

Table 4. Bond lengths in 1*H*-tetrazole (1HT), 1-methyltetrazole (1MT) and 5-methyltetrazole (5MT) (\AA)

	1HT	1MT	5MT
N1—N2	1.332 (2)	1.344 (2)	1.342 (3)
N2—N3	1.295 (3)	1.299 (2)	1.285 (3)
N3—N4	1.346 (3)	1.360 (2)	1.358 (3)
N4—C1	1.315 (2)	1.315 (2)	1.316 (3)
C1—N1	1.308 (2)	1.331 (2)	1.332 (2)
N1—C		1.455 (2)	
C1—C2			1.473 (3)

The structure was solved by direct methods and difference Fourier synthesis and refined by full-matrix least-squares methods, with anisotropic displacement parameters for all non-H atoms. H atoms were located using a difference electron-density map and were included in the structure factor calculation but not refined.

Data collection: *CRYSTAN-GM* (Mackay *et al.*, 1995). Cell refinement: *CRYSTAN-GM*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1103). Services for accessing these data are described at the back of the journal.

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Crystallographic evidence for the electronic distribution in (2,4-cyclopentadien-1-yl-idenehydrazono)triphenylphosphorane

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Abstract

The title compound, C₂₃H₁₉N₂P, can be graphically represented by several canonical forms. Its crystal structure analysis shows a clear bond alternation in the cyclopentadiene ring, which continues in the azo substructure, indicating that the resonance form containing the non-aromatic neutral cyclopentadienylidene moiety describes the actual hybrid form better than other 'inner ionic' resonance forms containing the aromatic anionic cyclopentadienylic portion. The preference for an *s-transoid*