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3,4,5-Trimethyl-1,2,4-triazole trihydrate

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.001 Å
R factor = 0.049
wR factor = 0.149
Data-to-parameter ratio = 41.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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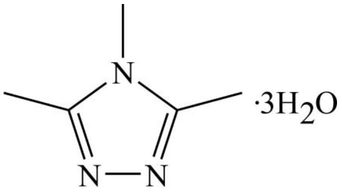
The title compound, $C_5H_9N_3 \cdot 3H_2O$, features an extensive network of hydrogen bonding, but is otherwise unexceptional. The structure was determined from data collected on a non-merohedrally twinned crystal.

Comment

The synthesis of 3,4,5-trimethyl-1,2,4-triazole trihydrate, (I), was reported over 70 years ago (Meyer, 1933). In fact, the product isolated by this method was 3,5-dimethyl-1,2,4-triazole trihydrate, a composition identical to (I) (Duffin *et al.*, 1954). Anhydrous 3,5-dimethyl-1,2,4-triazole was attainable by drying *in vacuo* over P_2O_5 followed by recrystallization from anhydrous benzene; however, it readily reverts to the hydrate in the presence of air (Duffin *et al.*, 1959).



(I)

The crystal of (I) selected for the diffraction experiment was found to be non-merohedrally twinned, *vide infra*; nonetheless, after the orientation matrices were determined and with the twin law and matrix in hand, a good-quality refinement was obtained. That 3,4,5-trimethyl-1,2,4-triazole crystallized as the trihydrate of 3,5-dimethyl-1,2,4-triazole is not surprising given the conditions under which the crystals grew. A *Mogul* geometry check showed all non-hydrogen bond angles and distances to be normal (Bruno *et al.* 2004). The two most similar molecules identified in the Cambridge Structural

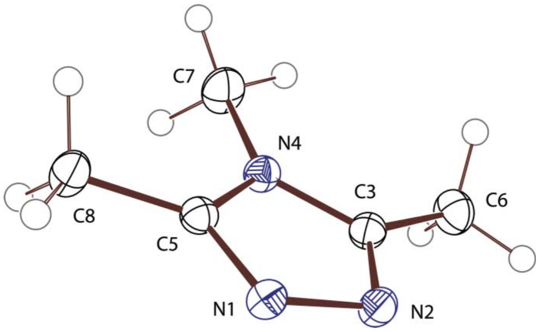


Figure 1
The molecular structure of 3,4,5-trimethyl-1,2,4-triazole, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Water molecules have been omitted for clarity.

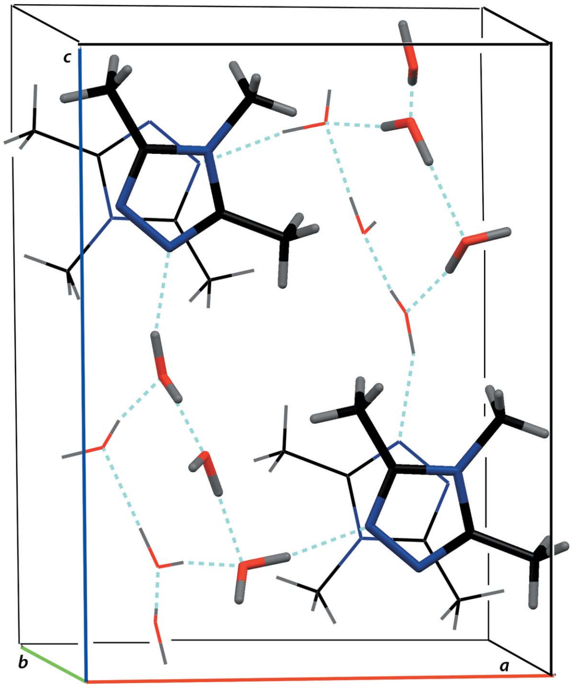


Figure 2
A view of the unit cell contents, showing the relative volume occupied by the main residue and water molecules. Dashed lines indicate hydrogen-bonding interactions.

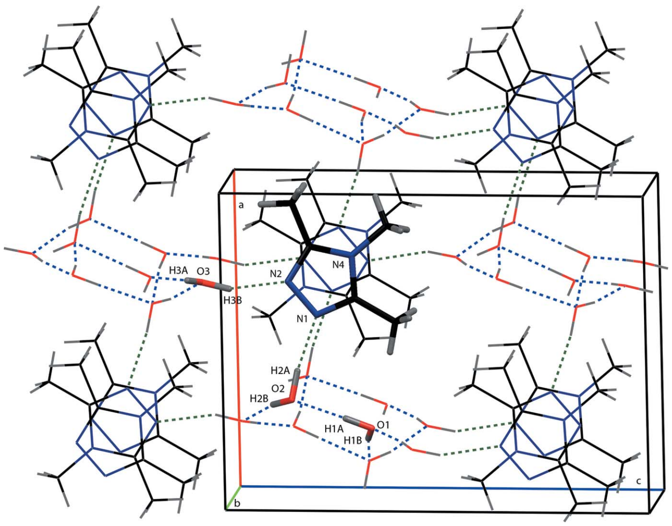


Figure 3
A view nearly orthogonal to the *ac* plane, highlighting the extensive hydrogen-bonding network. Triazole-to-water hydrogen bonds are indicated by dark-green dashed lines, and water-to-water hydrogen bonds are indicated by blue and cyan dashed lines.

database (Version 5.28; Allen, 2002) are 4-methyl-4*H*-1,2,4-triazole (Palmer & Parsons, 1996) and 3,5-bis(phenylethynyl)-4-*n*-propyl-1,2,4-triazole (Yasuda *et al.*, 2005). Comparison of the corresponding parameters in the two molecules to those in the title compound show them to be nearly identical within experimental error.

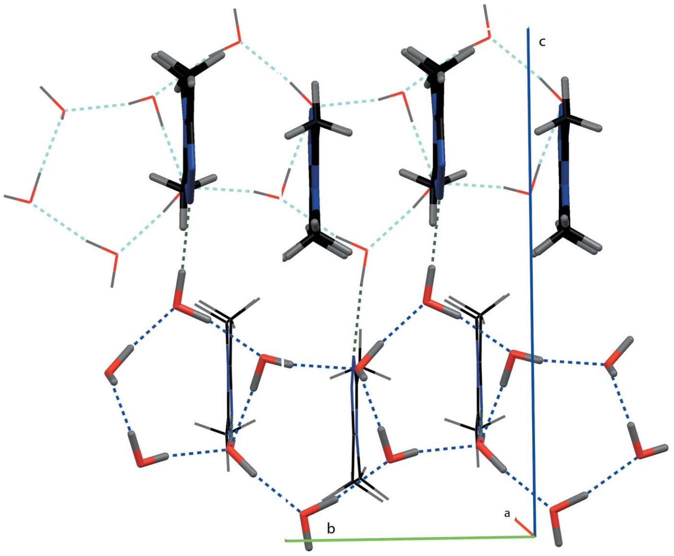


Figure 4
A view nearly orthogonal to the *bc* plane, highlighting the array of hydrogen-bonded water molecules forming pentagons. Hydrogen bonds are indicated as for Fig. 3.

The triazole molecules stack with the non-H atoms residing in the *ac* plane and along the *b* axis 2_1 screw axes, which run through the center of the triazole rings. The triazole molecules (Fig. 1) are accompanied in the unit cell by a substantial amount (33 mass %) of water, which fills channels running parallel to the stacks of the triazole molecules (Fig. 2).

Not surprisingly, the water molecules are heavily interconnected by hydrogen bonds, both with each other and with the triazole N atoms. The result is an infinite hydrogen-bonding network (Fig. 3). Each triazole is connected by N1 and N2 acceptor atoms to two donor water molecules via H2*A* and H3*B* (Fig. 3, dark-green dashed lines). Each water molecule is involved in hydrogen bonding to at least two other water molecules (Fig. 3, blue dashed lines). They form 'annellated' five-membered hydrogen-bonded rings that extend infinitely along the *b* axis (Fig. 4, blue and cyan dashed lines). The hydrogen-bonding distances and angles are all within usual ranges for such interactions (Table 1).

Experimental

During the preparation and subsequent high-temperature distillation of 3,5-dimethyl-1,2,4-triazole from acetamide and hydrazine hydrate using a literature method (Jones & Rees, 1969), the oil bath inadvertently caught fire. The fire was extinguished and the process was aborted; however, the 500 ml single-neck round-bottom reaction flask containing most of the reaction components was capped with a rubber septum and placed in storage, where it sat for a period of approximately three years. After this period, cm-long colourless needles were observed protruding out of the roughly 200 g of tan residue. Several crystals were harvested and one was selected and trimmed for the single-crystal X-ray diffraction experiment. Once the structure was determined to be that of a compound known for over 70 years (Meyer, 1933), no further characterization was carried out.

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Crystal data

$C_5H_9N_3 \cdot 3H_2O$
$M_r = 165.2$
Monoclinic, $P2_1/n$
$a = 10.0587\ (4)$ Å
$b = 6.5923\ (2)$ Å
$c = 13.4209\ (5)$ Å
$\beta = 91.183\ (1)^\circ$
$V = 889.75\ (6)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.1$ mm^{-1}
$T = 100\ (2)$ K
$0.38 \times 0.36 \times 0.23$ mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS* in *SAINT-Plus*; Bruker, 2003)
$T_{\min} = 0.966$, $T_{\max} = 0.977$
17695 measured reflections
5341 independent reflections
3958 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.149$
$S = 1.02$
5341 reflections
128 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2B···O3$^{\rm i}$	0.904 (13)	1.786 (13)	2.6804 (9)	169.6 (10)
O3—H3A···O1	0.923 (15)	1.822 (14)	2.7349 (10)	169.7 (12)
O2—H2A···N1$^{\rm ii}$	0.926 (14)	1.878 (14)	2.7974 (10)	171.2 (11)
O1—H1A···O2$^{\rm iii}$	0.908 (14)	1.890 (15)	2.7971 (9)	176.4 (13)
O3—H3B···N2$^{\rm iv}$	0.915 (18)	1.92 (2)	2.7959 (10)	159.9 (16)
O1—H1B···O2	0.800 (15)	1.978 (15)	2.7700 (9)	170.3 (14)

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x, y, z+1$.

The crystals under investigation were found to be non-merohedrally twinned, with a minor component of 0.1350 (6). H atoms attached to O atoms were identified in a difference Fourier synthesis and refined with isotropic displacement parameters; refined O—H distances are in Table 1. Methyl-group H atoms were included in the refinement in the riding-model approximation with torsion angles refined from the electron density, and with isotropic displacement parameters fixed at $1.2U_{\rm eq}$ of the parent atom (C—H = 0.98 Å).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2007).

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