Crystal structure of methyl 2-[5-(2-hydroxyphenyl)-2*H*-tetrazol-2-yl]acetate

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The title compound, $C_{10}H_{10}N_4O_3$, was synthesized by the esterification of hydroxyphenyl tetrazole. There is an intramolecular O—H$\cdots$N hydrogen bond present involving the hydroxy group and the tetrazole ring. The tetrazole ring is inclined to the phenol ring by 2.85 (13)°, while the methyl acetate group is almost normal to the tetrazole ring, making a dihedral angle of 82.61 (14)°. In the crystal, molecules are linked by pairs of C—H$\cdots$O hydrogen bonds, forming inversion dimers. Within the dimers, the phenol rings are linked by offset π–π interactions [intercentroid distance = 3.759 (2) Å]. There are no further significant intermolecular interactions present in the crystal. The hydroxy group is disordered about positions 2 and 6 on the benzene ring, with a refined occupancy ratio of 0.531 (5):0.469 (5).

1. Chemical context

Tetrazole ligands are useful building blocks for the construction of high-dimensional metal–organic frameworks by providing various binding modes toward metal centers (Karaghiosoff *et al.*, 2009; Liu *et al.*, 2013). Recently, we have used 5-(2-hydroxyphenyl)tetrazole as a chelating multidentate ligand and reported several interesting compounds (Park *et al.*, 2015; 2014). It provides strong [N,O] chelation to metal centers with various additional binding modes. As part of a project on the study of the substitution effects on the tetrazole ring on the self-assembly behaviour in solution, as well as in the solid state, we have synthesized a number of substituted hydroxyphenyl tetrazole complexes. The substitution of the tetrazole group may promote supramolecular interaction by weak interactions, such as hydrogen bonding. The reaction between hydroxyphenyl tetrazole and bromo acetate methyl ester in the presence of potassium carbonate gave three isomeric products. Using column chromatography, the major product was isolated and its molecular structure was determined unambiguously by X-ray crystallography. We report herein, the synthesis and crystal structure of this compound.
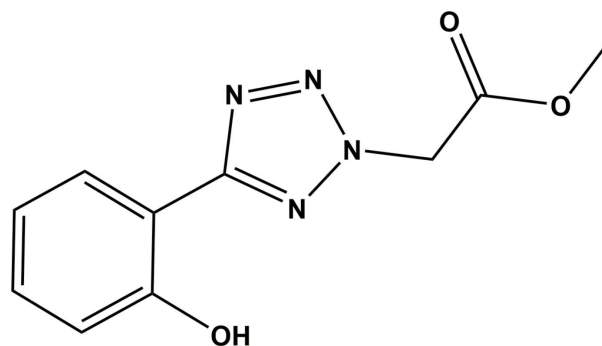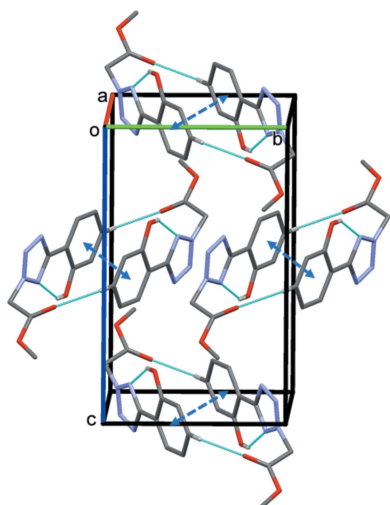
Table 1
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1—H1$\cdots$N1	0.84	1.91	2.659 (4)	148
C5—H5$\cdots$O3[i]	0.95	2.57	3.472 (3)	158

Symmetry code: (i) $-x + 1, -y, -z + 1$.

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The structure analysis confirms the nature of the major product of the reaction, which yielded three isomeric compounds as described in Section 5, *Synthesis and crystallization*. The title molecule consists of a tetrazole ring (N1–N4/C1) and a phenol ring (C2–C7), which are connected by an intramolecular O—H$\cdots$N hydrogen bond (Fig. 1, Table 1) and inclined to one another by 2.85 (13)°. The planar methyl acetate group [O2/O3/C8–C10; maximum deviation of 0.037 (2) Å for atom O2] is inclined to the tetrazole ring by 82.61 (14)°.

3. Supramolecular features

In the crystal, the molecules are linked by pairs of C—H$\cdots$O hydrogen bonds, forming inversion dimers with an $R_2^2(22)$ loop (Table 1, Fig. 2). Within the dimers, the phenol rings are linked by offset π–π interactions [$Cg\cdots Cg^i$ = 3.759 (2) Å, interplanar distance = 3.526 (1) Å, slippage 1.305 Å; Cg is the centroid of the C2–C7 phenol ring, symmetry code: (i) $-x + 1, -y, -z + 1$]. There are no further significant intermolecular interactions present in the crystal.

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, update May 2017; Groom *et al.*, 2016) for the methyl 2-(5-phenyl-2*H*-tetrazol-2-yl)acetate skeleton revealed only two hits, *viz.* ethyl (*Z*)-3-phenyl-2-(5-phenyl-2*H*-tetrazol-2-yl)-2-propenoate (SAKVIM; Ramazani *et al.*, 2017) and methyl (5-phenyl-2*H*-tetrazol-2-yl)acetate (WUKNUN; Saeed *et al.*,
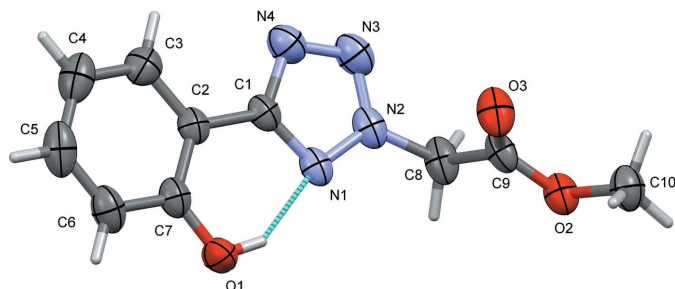

Figure 1
A view of the molecular structure of the title compound, with the atom labelling and 30% probability displacement ellipsoids. The intramolecular O—H$\cdots$N hydrogen bond (see Table 1) is indicated by a dashed line. Only the major component of the disordered OH group, in position 2, is shown.
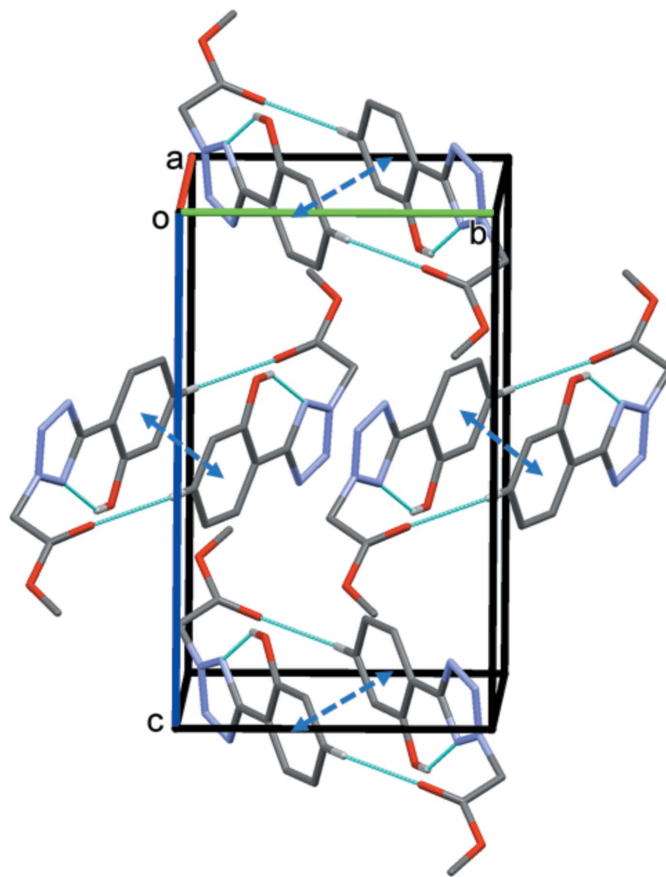

Figure 2
A view along the *a* axis of the crystal packing of the title compound. The intra- and intermolecular hydrogen bonds (see Table 1) are indicated by dashed lines. The offset π–π interactions are shown as dashed double arrows. Only H atoms H1 and H5, and the major component of the disordered OH group in position 2, have been included.

2015). In WUKNUN, the 5-phenyl substituent is inclined to the tetrazole ring by 3.89 (7)°, compared to 2.85 (13)° in the title compound. In contrast, the corresponding dihedral angle in SAKVIM is 19.97 (16)°. The methyl/ethyl acetate groups are inclined to the plane of the tetrazole ring by 84.99 (7)° in WUKNUN and 84.57 (7)° in SAKVIM, similar to the value observed in the title compound, *viz.* 82.61 (14)°.

5. Synthesis and crystallization

The synthesis of the title compound is illustrated in Fig. 3. 2-(2*H*-Tetrazol-5-yl)phenol (100 mg, 0.62 mmol) and potassium carbonate (85.0 mg, 0.62 mmol) were dissolved in acetonitrile at 273 K while stirring for 30 min. To the resulting solution methyl 2-bromoacetate (207 µl, 2.18 mmol) was added and stirring was continued for 24 h. The white solid that was obtained was filtered and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel using ether:hexane (2:3) as eluent. Three isomeric compounds were obtained, as shown in Fig. 3. The major product (I) (yield = 59%), was recrystallized in dichloromethane and yielded needle-like colourless crystals of the title compound. Spectroscopic data: ^{1}H NMR (CDCl$_3$,
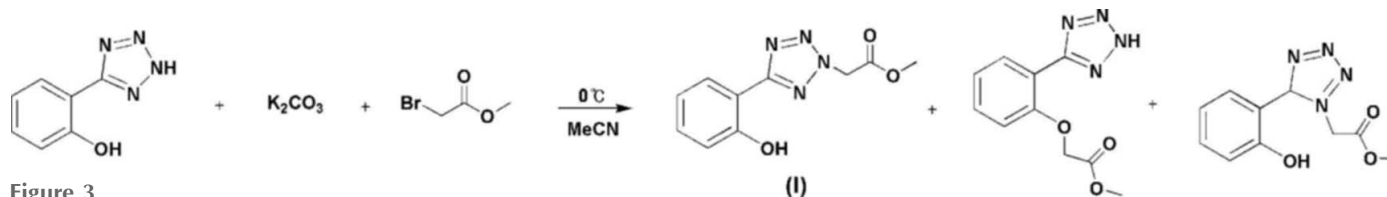
Figure 3
Reaction scheme for the synthesis of the title compound, (I).

400MHz): δ = 9.59 (s, 1H, OH), 8.06 (d, 1H, Ph), 7.41 (t, 1H, Ph), 7.11 (d, 1H, Ph), 6.99 (t, 1H, Ph), 5.51 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): 165.06, 164.68, 156.42, 132.44, 127.50, 120.06, 117.62, 53.41, 53.38 ppm.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydroxy group is disordered about positions 2 and 6 on the phenol ring, with a refined occupancy ratio of 0.531 (5):0.469 (5). All the H atoms were included in calculated positions using a riding model: O—H = 0.84 Å, C-H = 0.95–1.00 Å with U_{iso}(H) = 1.5 U_{eq}(O-hydroxyl, C-methyl) and 1.2U_{eq}(C) for other H atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_{10}N_4O_3$
M_r	234.22
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	10.060 (2), 8.2538 (17), 13.536 (3)
β (°)	104.479 (10)
V (Å^3)	1088.2 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.11
Crystal size (mm)	$0.15 \times 0.10 \times 0.10$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.987, 0.989
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14003, 2372, 1252
R_{int}	0.044
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.642
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.137, 1.02
No. of reflections	2372
No. of parameters	167
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.14, −0.17

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

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Crystal structure of methyl 2-[5-(2-hydroxyphenyl)-2*H*-tetrazol-2-yl]acetate

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Methyl 2-[5-(2-hydroxyphenyl)-2*H*-tetrazol-2-yl]acetate

Crystal data

$C_{10}H_{10}N_4O_3$	$F(000) = 488$
$M_r = 234.22$	$D_x = 1.430$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.060$ (2) Å	Cell parameters from 3134 reflections
$b = 8.2538$ (17) Å	$\theta = 2.9$–24.3°
$c = 13.536$ (3) Å	$\mu = 0.11$ mm^{-1}
$\beta = 104.479$ (10)°	$T = 100$ K
$V = 1088.2$ (4) Å^3	Needle, colourless
$Z = 4$	$0.15 \times 0.10 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer	2372 independent reflections
	1252 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.044$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$\theta_{max} = 27.2°$, $\theta_{min} = 2.1°$
	$h = -12 \rightarrow 12$
$T_{min} = 0.987$, $T_{max} = 0.989$	$k = -10 \rightarrow 10$
14003 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.057$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.137$	
$S = 1.01$	H-atom parameters constrained
2372 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 0.3171P]$ where $P = (F_o^2 + 2F_c^2)/3$
167 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.14$ e Å^{-3}
	$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.3781 (3)	0.2337 (4)	0.3644 (3)	0.0745 (14)	0.531 (5)
H1	0.4534	0.2755	0.3623	0.112*	0.531 (5)
O2	0.92819 (16)	0.46762 (19)	0.26859 (14)	0.0718 (5)	
O3	0.92563 (18)	0.2756 (2)	0.38419 (16)	0.0879 (6)	
O1A	0.5939 (5)	0.1877 (6)	0.7094 (3)	0.1031 (19)	0.469 (5)
H1A	0.6557	0.2377	0.6900	0.155*	0.469 (5)
N1	0.61929 (19)	0.3786 (2)	0.43476 (16)	0.0618 (5)	
N2	0.7415 (2)	0.4500 (2)	0.46016 (19)	0.0679 (6)	
N3	0.8043 (2)	0.4384 (3)	0.5571 (2)	0.0890 (7)	
N4	0.7203 (2)	0.3567 (3)	0.59958 (17)	0.0826 (7)	
C1	0.6085 (2)	0.3209 (3)	0.5240 (2)	0.0574 (6)	
C2	0.4922 (2)	0.2276 (2)	0.53816 (19)	0.0555 (6)	
C3	0.4899 (3)	0.1677 (3)	0.6336 (3)	0.0749 (7)	
H3	0.5638	0.1911	0.6908	0.090*	0.531 (5)
C4	0.3811 (4)	0.0744 (3)	0.6462 (3)	0.0916 (10)	
H4	0.3810	0.0334	0.7117	0.110*	
C5	0.2743 (3)	0.0412 (3)	0.5647 (3)	0.0913 (10)	
H5	0.2001	−0.0237	0.5734	0.110*	
C6	0.2733 (3)	0.1010 (3)	0.4701 (3)	0.0831 (8)	
H6	0.1978	0.0790	0.4137	0.100*	
C7	0.3818 (3)	0.1929 (3)	0.4565 (2)	0.0652 (7)	
H7	0.3808	0.2330	0.3905	0.078*	0.469 (5)
C8	0.8045 (3)	0.5246 (3)	0.3866 (2)	0.0778 (8)	
H8A	0.8619	0.6170	0.4189	0.093*	
H8B	0.7322	0.5670	0.3288	0.093*	
C9	0.8923 (2)	0.4048 (3)	0.3474 (2)	0.0635 (7)	
C10	1.0223 (3)	0.3749 (3)	0.2257 (2)	0.0834 (8)	
H10A	1.0402	0.4334	0.1674	0.125*	
H10B	0.9817	0.2691	0.2031	0.125*	
H10C	1.1087	0.3594	0.2776	0.125*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.063 (2)	0.086 (3)	0.071 (3)	−0.0122 (18)	0.0098 (17)	0.0043 (19)
O2	0.0666 (11)	0.0501 (10)	0.1035 (13)	0.0043 (8)	0.0303 (10)	0.0086 (10)
O3	0.0893 (13)	0.0446 (10)	0.1425 (17)	0.0147 (9)	0.0529 (12)	0.0194 (11)
O1A	0.127 (4)	0.118 (4)	0.062 (3)	0.006 (3)	0.018 (3)	0.011 (3)
N1	0.0533 (12)	0.0445 (11)	0.0897 (15)	0.0028 (10)	0.0215 (11)	−0.0002 (11)

N2	0.0570 (13)	0.0463 (12)	0.1035 (18)	0.0007 (10)	0.0260 (13)	−0.0040 (12)
N3	0.0684 (15)	0.0838 (18)	0.111 (2)	−0.0131 (14)	0.0151 (15)	−0.0115 (16)
N4	0.0699 (15)	0.0835 (16)	0.0897 (17)	−0.0084 (13)	0.0113 (13)	−0.0090 (13)
C1	0.0534 (15)	0.0414 (12)	0.0779 (17)	0.0082 (11)	0.0172 (13)	−0.0068 (13)
C2	0.0568 (14)	0.0374 (12)	0.0754 (17)	0.0095 (11)	0.0225 (13)	−0.0017 (12)
C3	0.085 (2)	0.0605 (17)	0.082 (2)	0.0139 (15)	0.0271 (18)	0.0054 (16)
C4	0.118 (3)	0.0586 (18)	0.119 (3)	0.0109 (19)	0.069 (2)	0.0116 (18)
C5	0.096 (2)	0.0504 (17)	0.151 (3)	−0.0090 (16)	0.074 (2)	−0.015 (2)
C6	0.0686 (18)	0.0668 (18)	0.121 (3)	−0.0077 (15)	0.0376 (17)	−0.0194 (18)
C7	0.0604 (16)	0.0517 (15)	0.088 (2)	0.0008 (12)	0.0273 (15)	−0.0047 (14)
C8	0.0703 (16)	0.0433 (14)	0.130 (2)	0.0011 (12)	0.0439 (17)	0.0049 (15)
C9	0.0474 (13)	0.0384 (13)	0.106 (2)	−0.0044 (11)	0.0219 (13)	−0.0004 (14)
C10	0.0779 (18)	0.0708 (18)	0.110 (2)	0.0042 (15)	0.0398 (16)	−0.0052 (16)

Geometric parameters (Å, º)

O1—C7	1.282 (4)	N4—C1	1.351 (3)
O2—C9	1.315 (3)	C1—C2	1.452 (3)
O2—C10	1.447 (3)	C2—C7	1.387 (3)
O3—C9	1.190 (3)	C2—C3	1.388 (3)
O1A—C3	1.280 (5)	C3—C4	1.383 (4)
N1—C1	1.328 (3)	C4—C5	1.362 (4)
N1—N2	1.329 (3)	C5—C6	1.370 (4)
N2—N3	1.310 (3)	C6—C7	1.378 (3)
N2—C8	1.445 (3)	C8—C9	1.508 (3)
N3—N4	1.319 (3)		
C9—O2—C10	117.19 (18)	O1A—C3—C4	119.1 (4)
C1—N1—N2	101.8 (2)	O1A—C3—C2	119.9 (3)
N3—N2—N1	114.2 (2)	C4—C3—C2	120.7 (3)
N3—N2—C8	122.4 (2)	C5—C4—C3	120.0 (3)
N1—N2—C8	123.2 (2)	C4—C5—C6	120.3 (3)
N2—N3—N4	105.9 (2)	C5—C6—C7	120.1 (3)
N3—N4—C1	106.5 (2)	O1—C7—C6	116.2 (3)
N1—C1—N4	111.6 (2)	O1—C7—C2	122.9 (3)
N1—C1—C2	124.2 (2)	C6—C7—C2	120.7 (3)
N4—C1—C2	124.2 (2)	N2—C8—C9	111.09 (19)
C7—C2—C3	118.1 (2)	O3—C9—O2	126.0 (2)
C7—C2—C1	121.0 (2)	O3—C9—C8	124.7 (2)
C3—C2—C1	120.8 (2)	O2—C9—C8	109.3 (2)

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1⋯N1	0.84	1.91	2.659 (4)	148
C5—H5⋯O3[i]	0.95	2.57	3.472 (3)	158

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.