Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4-Nitro-2-(1*H*-tetrazol-1-yl)phenol

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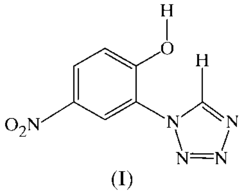
Received 17 April 2001
Accepted 17 July 2001

There are two symmetry-independent molecules in the unit cell of the title compound, $C_7H_5N_5O_3$. The tetrazole and phenyl rings are essentially planar and are not coplanar in either molecule [dihedral angles 30.2 (1) and 7.0 (1)°]. In the structure, four molecules are connected by O—H···N bridges, forming four-membered molecular aggregates which are linked together by a complex three-dimensional hydrogen-bond network.

Comment

Monosubstituted 1-aryltetrazoles have attracted considerable theoretical and experimental interest. On the one hand, they are used as valuable intermediates in the synthesis of arylcyanamides (Gaponik *et al.*, 1990) and different nitrogen-containing heterocycles (Voitekhovich *et al.*, 2001), while on the other hand, they have attracted interest as models for investigation of the interaction between tetrazole and phenyl rings. Only the structures of 1-phenyltetrazole (Matsunaga *et al.*, 1999) and 1-(2,4,6-trimethylphenyl)tetrazole (Lyakhov *et al.*, 2000) have been described previously. In this paper, we present the crystal structure of a new compound, namely 4-nitro-2-(1*H*-tetrazol-1-yl)phenol, (I) (Fig. 1). There are two symmetry-independent molecules in the structure, denoted *A* and *B* hereafter.



(I)

The tetrazole rings of molecules *A* and *B* have very similar geometries and are planar to within 0.004 (2) and 0.005 (2) Å, respectively. The endocyclic angles are in the ranges 105.5 (1)–111.1 (1) and 106.1 (1)–110.6 (1)° for molecules *A* and *B*, respectively. The N1—N2 and N3—N4 bonds are similar and longer than N2—N3, while the C5—N1 bond is longer than C5—N4 in both molecules (Table 1). All the formal single endocyclic bonds are considerably shorter than those usually found for normal single bonds, but the formal double bonds are somewhat longer than normal double bonds (*International Tables for Crystallography*, 1992, Vol. C, pp. 707–791). This suggests that there is some conjugation in the tetrazole rings of (I); however, significant differences in the endocyclic bond lengths show that there is still considerable localization of charge within them.

The bond distances and angles in the phenyl-ring fragments of (I) are consistent with those observed previously. The rings are nearly planar to within 0.009 (1) and 0.008 (1) Å for molecules *A* and *B*, respectively.

The phenyl and tetrazole rings are not coplanar in either molecule, the dihedral angles between them being 30.2 (1) and 7.0 (1)° in molecules *A* and *B*, respectively. To compare these values with that of a free molecule of (I), an *ab initio* calculation of a single molecule in the 6–311G** basis set was carried out using the *GAMESS* program (Schmidt *et al.*, 1993). Geometry optimization with respect to all variables results in a dihedral angle between the phenyl and tetrazole rings of 39.6°. It should be noted that in the crystal of 1-phenyltetrazole, the dihedral angle between the rings is 11.8 (1)° (Matsunaga *et al.*, 1999), whereas an angle of 38.6° was obtained from an MP2/6–31G* calculation for a free molecule of 1-phenyltetrazole (Matsunaga *et al.*, 1999). The introduction of an *ortho*-substituent on the phenyl ring must result in increased steric hindrance compared with 1-phenyltetrazole and, as a result, the dihedral angle between the rings increases. Such a situation is also seen in the crystal structure of 1-(2,4,6-trimethylphenyl)tetrazole, where the dihedral angle is 69.07 (9)° (Lyakhov et al., 2000), and also in molecule *A* of (I). In the case of molecule *B* of (I), a rather small dihedral angle is found. Taking these results into account, it may be presumed that the decrease in the dihedral angle in the crystal is due to molecular packing. In the structure of (I), this effect is larger for molecule *B* than for molecule *A*.

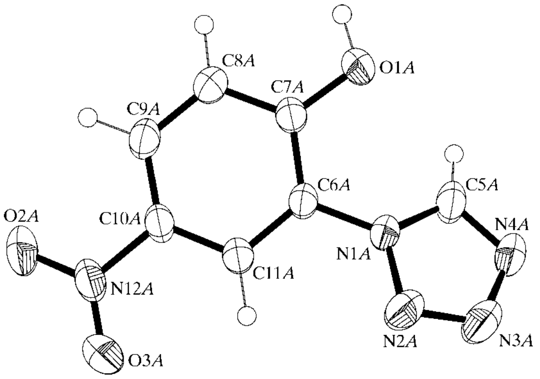


Figure 1
ORTEP-3 drawing (Farrugia, 1997) of molecule *A* of (I) with the atom-numbering scheme; for molecule *B*, substitute the *A* suffixes with *B*. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

From an inspection of the packing of the molecules in (I), the following may be noted (Fig. 3). There are two types of hydrogen bonds (Table 2), O1*A*—H1*A*···N4*B* and O1*B*—H1*B*···N4*A*, between molecules *A* and *B*, resulting in the formation of four-membered aggregates in the structure (Fig. 2). C8*B*—H8*B*···N3*A* interactions may be considered as additional weak hydrogen bonds between molecules *A* and *B* in the four-membered aggregates. Connection of these aggregates is achieved mainly through C9*A*—H9*A*···N2*B* hydrogen bonds (N2*A* does not form similar bonds). There are also C—H···O contacts (Desiraju, 1996) between the nitro O atoms and the H atoms of the phenyl rings, thereby forming additional connections between the aggregates. The molecules in the structure of (I) are thus linked together by a complex three-dimensional hydrogen-bond network.

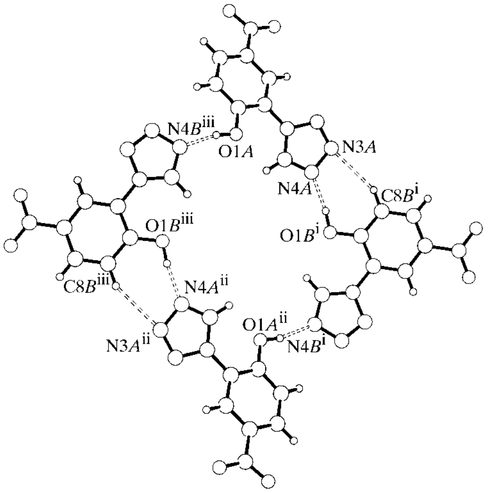


Figure 2
[100] view of the four-membered aggregate in the structure of (I). Hydrogen-bond bridges between the molecules are shown by dashed lines. [Symmetry codes: (i) $-x, -y, 2-z$; (ii) $-x-1, 1-y, 2-z$; (iii) $x-1, y+1, z$.]

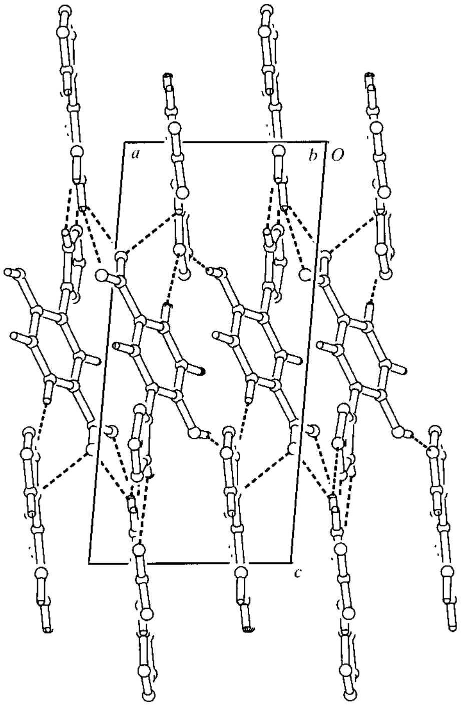


Figure 3
Packing diagram of the title compound.

Experimental

The title compound was prepared by heterocyclization of 2-amino-4-nitrophenol with ethyl orthoformate and sodium azide in acetic acid (Voitekhovich *et al.*, 2001). Single crystals were grown by slow crystallization from an acetonitrile solution.

Crystal data

$C_7H_5N_5O_3$
$M_r = 207.16$
Triclinic, $P\overline{1}$
$a = 7.116$ (2) Å
$b = 9.452$ (2) Å
$c = 13.895$ (3) Å
$\alpha = 86.43$ (2)°
$\beta = 84.17$ (2)°
$\gamma = 68.42$ (2)°
$V = 864.3$ (4) Å^3
$Z = 4$
$D_x = 1.592$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.5$–19.8°
$\mu = 0.13$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.54 × 0.40 × 0.30 mm

Data collection

Nicolet *R*3*m* four-circle diffractometer
$\omega/2\theta$ scans
5619 measured reflections
5062 independent reflections
3704 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 30.1°$
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 13$
$l = -19 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.143$
$S = 1.04$
5062 reflections
311 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0837P)^2 + 0.0881P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}

H-atom positions were found from the ΔF map and all associated parameters were refined freely [C—H = 0.92 (2)–0.99 (2) Å].

Table 1
Selected geometric parameters (Å, °).

N1*A*—C5*A*	1.327 (2)	N1*B*—C5*B*	1.334 (2)
N1*A*—N2*A*	1.346 (2)	N1*B*—N2*B*	1.350 (2)
N1*A*—C6*A*	1.427 (2)	N1*B*—C6*B*	1.431 (2)
N2*A*—N3*A*	1.290 (2)	N2*B*—N3*B*	1.287 (2)
N3*A*—N4*A*	1.350 (2)	N3*B*—N4*B*	1.343 (2)
N4*A*—C5*A*	1.300 (2)	N4*B*—C5*B*	1.307 (2)
C5*A*—N1*A*—N2*A*	108.0 (1)	C5*B*—N1*B*—N2*B*	107.2 (1)
N3*A*—N2*A*—N1*A*	105.9 (1)	N3*B*—N2*B*—N1*B*	106.9 (1)
N2*A*—N3*A*—N4*A*	111.1 (1)	N2*B*—N3*B*—N4*B*	110.6 (1)
C5*A*—N4*A*—N3*A*	105.5 (1)	C5*B*—N4*B*—N3*B*	106.1 (1)
N4*A*—C5*A*—N1*A*	109.5 (1)	N4*B*—C5*B*—N1*B*	109.2 (1)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···N4*B*^{i}	0.91 (3)	1.78 (3)	2.665 (2)	165 (2)
O1*B*—H1*B*···N4*A*^{ii}	0.93 (2)	1.78 (2)	2.703 (2)	171 (2)
C5*A*—H5*A*···O2*B*^{iii}	0.92 (3)	2.55 (2)	3.234 (2)	131 (2)
C5*B*—H5*B*···O3*B*^{iv}	0.96 (2)	2.56 (2)	3.283 (2)	132 (1)
C8*B*—H8*B*···O3*A*^{v}	0.98 (2)	2.57 (2)	3.320 (2)	133 (1)
C8*B*—H8*B*···N3*A*^{ii}	0.98 (2)	2.56 (2)	3.465 (2)	153 (1)
C9*A*—H9*A*···N2*B*^{vi}	0.98 (2)	2.56 (2)	3.540 (2)	176 (2)
C9*B*—H9*B*···O2*A*^{v}	0.96 (2)	2.58 (2)	3.417 (2)	145 (2)
C11*B*—H11*B*···O2*A*^{vi}	0.94 (2)	2.53 (2)	3.191 (2)	128 (1)

Symmetry codes: (i) $x-1, 1+y, z$; (ii) $-x, -y, 2-z$; (iii) $-x, 1-y, 2-z$; (iv) $x, y-1, z$; (v) $x, y, 1+z$; (vi) $-x, 1-y, 1-z$.

Data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1080). Services for accessing these data are described at the back of the journal.

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