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Two derivatives of 5-aminotetrazole: 5-amino-1-phenyltetrazole and 5-amino-1-(1-naphthyl)tetrazole

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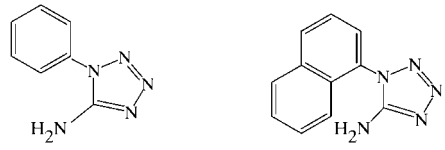
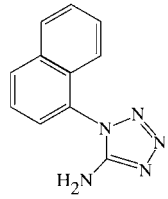
In the molecules of 5-amino-1-phenyltetrazole, $C_7H_7N_5$, (I), and 5-amino-1-(1-naphthyl)tetrazole, $C_{11}H_9N_5$, (II), the tetrazole rings and aryl fragments are not coplanar; corresponding dihedral angles are 50.58 (5) and 45.19 (7)° for the two independent molecules of (I), and 64.14 (5)° for (II). Intermolecular N—H···N hydrogen bonds between the amino groups and tetrazole N atoms are primarily responsible for formation of two-dimensional networks extending parallel to the *bc* plane in both compounds. The presence of the amino group has a distinct effect on the geometry of the tetrazole rings in each case.

Comment

5-Amino-1-aryltetrazoles have attracted much attention because of their biological activity (Wittenberger, 1994; Schelenz, 2000, and references therein). Thus, 5-amino-1-phenyltetrazole, (I), reveals anti-inflammatory, muscle relaxation and central nervous system (CNS) depressant properties. Recently, the algistatic activity of 5-amino-1-aryltetrazoles, including 5-amino-1-(1-naphthyl)tetrazole, (II), was reported (Schelenz, 2000; Katritzky *et al.*, 2001). Although a large body of information concerned with synthesis techniques and biological activities of 5-amino-1-aryltetrazoles is available, no systematic investigation of their structures has been performed; only one compound, namely 1-(4-methoxyphenyl)-5-(phenylamino)tetrazole (Brigas *et al.*, 2001), was found in the Cambridge Structural Database (CSD; Version 5.24, November 2002 release; Allen, 2002) in a search for 5-amino-1-aryltetrazoles. However, structural information might be very important for understanding the mechanisms of biological activity of these compounds. We present here the structures of two 5-amino-1-aryltetrazoles, the above-mentioned compounds (I) and (II). The asymmetric unit of (I) consists of two independent molecules, which are denoted *A* and *B*.

The tetrazole rings are planar to within 0.0024 (8) and 0.0014 (9) Å for molecules *A* and *B*, respectively, of (I), and 0.0026 (9) Å for (II). The tetrazole rings are not coplanar with the phenyl or naphthyl fragments in their respective molecules. The dihedral angles between the least-squares planes of the tetrazole and aryl systems in (I) are 50.58 (5) and 45.19 (7)° for *A* and *B*, respectively, and 64.14 (5)° in (II).


(I) (II)


(II*a*)

The molecule of (II) may exist in two forms, namely the *s-trans*-(N^2)-conformer (II) and the *s-cis*-(N^2)-conformer (II*a*) (see scheme), which are related by rotational isomerism. Density functional theory (DFT) calculations of the relative energies of conformers (II) and (II*a*) in the gas phase, performed using the B3LYP model (Becke, 1993) and a standard 6-31G* basis set (Hehre *et al.*, 1972) with the *NWCHEM* package (Harrison *et al.*, 2002), showed that conformer (II*a*) is more stable by 2.29 kJ mol^{-1}. However, it is conformer (II) which occurs in the crystal structure. It seems probable that the magnitude of the crystal packing energy overlaps the energy difference for the *s-trans*-(N^2)- and *s-cis*-(N^2)-conformers.

The N5 atoms of the amino groups in (I) and (II) display features of sp^2 hybridization. The angle sums around these atoms are *ca* 349° for both molecules of (I) and *ca* 360° for (II) (Tables 1 and 3). In (I), the amino group atoms are located close to the adjacent tetrazole ring plane, with maximum deviations of 0.25 (2) (for atom H5*A* in molecule *A*) and

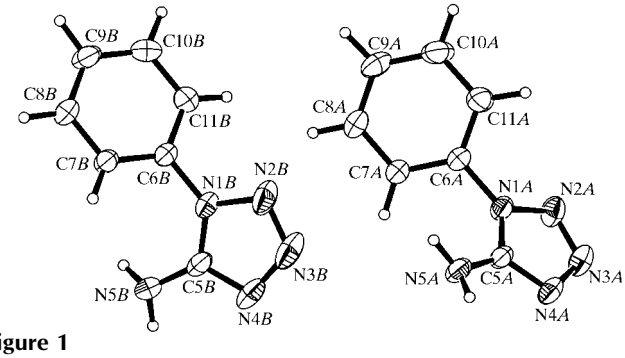


Figure 1
A view of the two independent molecules of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level.

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0.26 (2) Å (for atom H5*C* in molecule *B*). In (II), the corresponding maximum deviation of 0.06 (2) Å occurs for atom H5*A*. Moreover, the C5—N5 bond lengths in (I) and (II) (Tables 1 and 3) are close to those for C=N double bonds.

The corresponding bond lengths and angles of the tetrazole rings of (I) and (II) are very similar (Tables 1 and 3). Comparison of the tetrazole-ring characteristics of (I) and (II) with those of 5-aminotetrazole (Bray & White, 1979) did not reveal any influence of the aryl substitutents on the ring geometry. Taking into account the results of the X-ray investigation of 1-phenyltetrazole (Matsunaga *et al.*, 1999), it is found that substitution of the H atom at ring atom C5 by the amino group in the molecule of (I) results in a shortening of the N2=N3 bond by 0.019 Å, but elongation of the N4=C5 and N1—N2 bonds by 0.027 and 0.020 Å, respectively. The N1—C5 and N3—N4 bond lengths are unaffected by this substitution.

DFT calculations on 1-phenyltetrazole and 5-amino-1-phenyltetrazole, 1-(1-naphthyl)tetrazole and 5-amino-1-(1-naphthyl)tetrazole showed that introducing a 5-amino group shortened N2=N3 by 0.008 and 0.008 Å, elongated N4=C5 by 0.007 and 0.008 Å, and elongated N1—N2 by 0.019 and 0.020 Å in (I) and (II), respectively, in agreement with the results of the structure determination.

To clarify whether this is a general effect, we examined the tetrazole-ring geometries of 1-*R*-5-amino- and 1-*R*-5*H*-tetrazoles where *R* is a substituted alkyl or aryl group, using the CSD. As can be seen from Table 5, amino substitution tends to shorten N2=N3 and elongate N1—N2 and N4=C5, while there is no marked trend for N1—C5 and N3—N4. These results and those obtained in the present work allow us to consider the geometric influence of the amino group on features of the tetrazole rings of 5-aminotetrazoles.

The elongation of the C5=N4 and the shortening of the C5—NH_2 bonds relative to 'normal' C—N bond lengths, and the approximately trigonal planar geometry of the 5-amino N atoms in 5-aminotetrazoles agree with considerable bond conjugation in the H_2N—C5=N4 fragments. However, the mechanism whereby N1—N2 is elongated and N2=N3 shortened in 5-aminotetrazoles relative to 5*H*-tetrazoles is not clear and may be a topic of future investigations.

Both structures exhibit intermolecular N—H···N hydrogen bonds between the amino groups and atoms N3 and N4 of the tetrazole rings (Tables 2 and 4). These hydrogen bonds are responsible for the formation of polymeric two-dimensional networks parallel to the *bc* plane in (I) and (II). The networks are linked only by van der Waals interactions. The hydrogen-bonding motifs in (I) and (II) differ to some extent. In (I), each molecule *A* is hydrogen bonded to three neighbours, *viz*. one *A* and two *B* molecules, forming an eight-membered

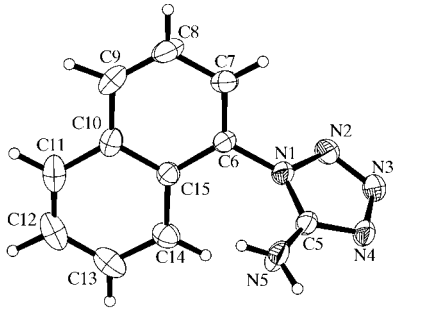

Figure 2
A view of (II), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level.

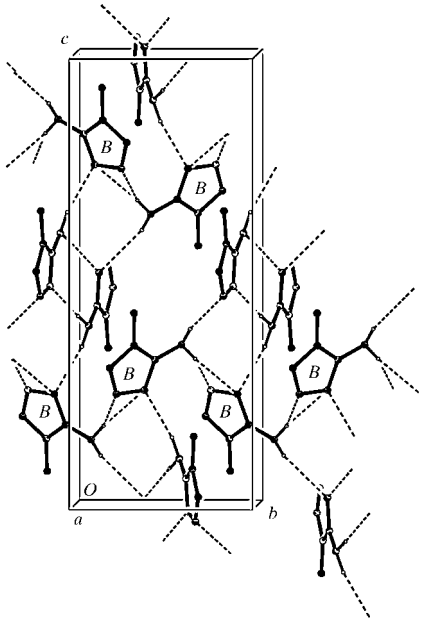

Figure 3
A fragment of the crystal structure of (I), showing the hydrogen-bonded two-dimensional network parallel to the *bc* plane. Dashed lines show N—H···N hydrogen bonds. Label '*B*' indicates molecules *B* (unlabelled molecules are *A*). For clarity, phenyl groups are represented by their bridgehead atoms.

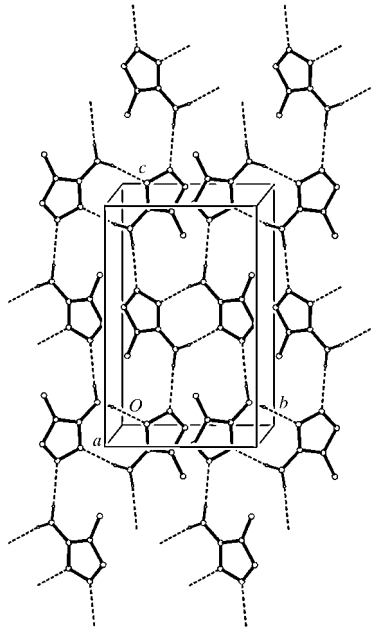

Figure 4
A fragment of the crystal structure of (II), showing the hydrogen-bonded two-dimensional network parallel to the *bc* plane. Dashed lines indicate N—H···N hydrogen bonds. For clarity, naphthyl groups are represented by their bridgehead atoms.

hydrogen-bonded ring by binding with molecule *A* (Fig. 3). Each molecule *B* is hydrogen bonded to four neighbours, *viz*. two *A* and two *B* molecules. All hydrogen bonds involving the amino groups of molecules *B* are bifurcated. In (II), each molecule is hydrogen bonded to three others, eight-membered hydrogen-bonded rings being formed by bonding to one molecule (Fig. 4). In addition to the two-dimensional network, the structure also contains non-classical C8—H8···N2 interactions.

Experimental

The title compounds, (I) and (II), were prepared from aniline and 1-naphthylamine, respectively, using the three-stage technique reported by Vorobiev *et al.* (2003). Single crystals of (I) and (II) suitable for analysis were grown by slow evaporation from a 2-propanol–acetonitrile solvent system (3:1) at room temperature.

Compound (I)

Crystal data

$C_7H_7N_5$
M_r = 161.18
Monoclinic, $P2_1/c$
a = 11.619 (3) Å
b = 7.342 (2) Å
c = 18.124 (3) Å
β = 92.202 (19)°
V = 1545.0 (6) Å^3
Z = 8
D_x = 1.386 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 18.8–21.3°
μ = 0.10 mm^{-1}
T = 293 (2) K
Rectangular prism, colourless
0.60 × 0.40 × 0.24 mm

Data collection

Nicolet *R*3*m* four-circle diffractometer
$\omega/2\theta$ scans
4745 measured reflections
4542 independent reflections
3154 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 30.1°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 10$
$l = -25 \rightarrow 25$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.145
S = 1.05
4542 reflections
274 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.1138P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.211 (9)

Table 1
Selected geometric parameters (Å, °) for (I).

N1*A*—C5*A*	1.3473 (15)	N1*B*—C5*B*	1.3407 (16)
N1*A*—N2*A*	1.3681 (14)	N1*B*—N2*B*	1.3651 (15)
N1*A*—C6*A*	1.4309 (13)	N1*B*—C6*B*	1.4265 (14)
N2*A*—N3*A*	1.2793 (16)	N2*B*—N3*B*	1.2840 (18)
N3*A*—N4*A*	1.3647 (18)	N3*B*—N4*B*	1.359 (2)
N4*A*—C5*A*	1.3288 (13)	N4*B*—C5*B*	1.3248 (14)
C5*A*—N5*A*	1.3374 (16)	C5*B*—N5*B*	1.3351 (19)
C5*A*—N1*A*—N2*A*	108.15 (9)	C5*B*—N1*B*—N2*B*	108.29 (10)
N3*A*—N2*A*—N1*A*	106.21 (11)	N3*B*—N2*B*—N1*B*	105.72 (13)
N2*A*—N3*A*—N4*A*	111.80 (10)	N2B—N3*B*—N4*B*	112.04 (12)
C5*A*—N4*A*—N3*A*	105.60 (10)	C5*B*—N4*B*—N3*B*	105.36 (12)
N4*A*—C5*A*—N1*A*	108.25 (11)	N4*B*—C5*B*—N1*B*	108.59 (13)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5*A*—H5*A*···N4*A*^{i}	0.89 (2)	2.194 (18)	3.0777 (17)	172 (2)
N5*A*—H5*B*···N4*B*^{ii}	0.91 (2)	2.209 (16)	3.0975 (16)	166.7 (13)
N5*B*—H5*C*···N4*A*^{iii}	0.84 (2)	2.50 (2)	3.2935 (19)	157 (2)
N5*B*—H5*C*···N3*A*^{iii}	0.84 (2)	2.62 (2)	3.423 (2)	161 (2)
N5*B*—H5*D*···N4*B*^{iv}	0.88 (2)	2.47 (2)	3.3493 (19)	173 (2)
N5*B*—H5*D*···N3*B*^{iv}	0.88 (2)	2.37 (2)	3.181 (2)	153 (2)

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

Compound (II)

Crystal data

$C_{11}H_9N_5$
M_r = 211.23
Monoclinic, $P2_1/c$
a = 12.176 (5) Å
b = 7.3611 (18) Å
c = 11.699 (3) Å
β = 93.85 (3)°
V = 1046.2 (6) Å^3
Z = 4
D_x = 1.341 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 17.8–21.0°
μ = 0.09 mm^{-1}
T = 293 (2) K
Rectangular prism, colourless
0.56 × 0.44 × 0.12 mm

Data collection

Nicolet *R*3*m* four-circle diffractometer
$\omega/2\theta$ scans
3326 measured reflections
3078 independent reflections
2055 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 30.1°
$h = -17 \rightarrow 17$
$k = -10 \rightarrow 0$
$l = 0 \rightarrow 16$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.207
S = 1.03
3078 reflections
181 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1428P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C5	1.3513 (19)	N3—N4	1.3628 (19)
N1—N2	1.3658 (17)	N4—C5	1.3277 (17)
N1—C6	1.4278 (17)	N5—C5	1.3309 (19)
N2—N3	1.2796 (19)		
C5—N1—N2	108.15 (12)	C5—N4—N3	105.40 (12)
N3—N2—N1	106.01 (12)	N4—C5—N1	108.27 (13)
N2—N3—N4	112.17 (12)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*A*···N3^{i}	0.84 (2)	2.25 (2)	3.077 (2)	168 (2)
N5—H5*B*···N4^{ii}	0.90 (2)	2.10 (2)	2.983 (2)	169 (2)
C8—H8···N2^{iii}	0.93 (3)	2.54 (3)	3.436 (2)	163 (2)

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

Table 5
Mean values of the tetrazole ring bond distances (Å) for 1-*R*-5*H*- and 1-*R*-5-aminotetrazoles (*R* = substituted alkyl or aryl) resulting from a CSD survey.

Bond	1-*R*-5*H*-tetrazoles (8 hits)	1-*R*-5-aminotetrazoles (5 hits)
N1—N2	1.347 (2)	1.361 (5)
N1—C5	1.333 (2)	1.333 (10)
N2═N3	1.294 (2)	1.273 (4)
N3—N4	1.354 (2)	1.360 (2)
N4═C5	1.307 (2)	1.319 (4)

Note: s.u. values on mean values are given in parentheses.

For both compounds, data collection: *R*3*m Software* (Nicolet, 1980); cell refinement: *R*3*m Software*; data reduction: *R*3*m Software*; structure solution: *SIR*97 (Altomare *et al.*, 1999); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1546). Services for accessing these data are described at the back of the journal.

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