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Two derivatives of 1,5-disubstituted tetrazoles: 1-(4-nitrophenyl)-1*H*-tetrazol-5-amine and {(*E*)-[1-(4-ethoxyphenyl)-1*H*-tetrazol-5-yl]iminomethyl}dimethylamine

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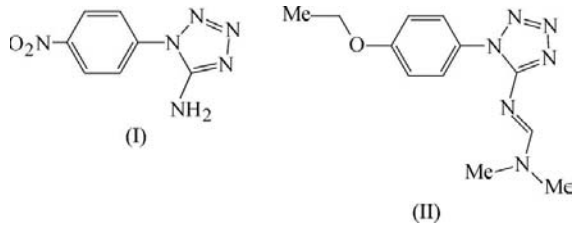
The geometric features of 1-(4-nitrophenyl)-1*H*-tetrazol-5-amine, $C_7H_6N_6O_2$, correspond to the presence of the essential interaction of the 5-amino group lone pair with the π system of the tetrazole ring. Intermolecular N—H···N and N—H···O hydrogen bonds result in the formation of infinite chains running along the [110] direction and involve centrosymmetric ring structures with motifs $R_2^2(8)$ and $R_2^2(20)$. Molecules of {(*E*)-[1-(4-ethoxyphenyl)-1*H*-tetrazol-5-yl]iminomethyl}-dimethylamine, $C_{12}H_{16}N_6O$, are essentially flattened, which facilitates the formation of a conjugated system spanning the whole molecule. Conjugation in the azomethine N=C—N fragment results in practically the same length for the formal double and single bonds.

Comment

5-Aminotetrazoles attract considerable attention because many of them reveal biological activity (Wittenberger, 1994; Schelenz, 2000; Katritzky *et al.*, 2003, and references therein). In particular, the use of 1-aryl-5-aminotetrazoles as anti-inflammatory agents has been described (Enkoji *et al.*, 1970), while 5-amino-1-nitrophenyltetrazoles have been found to be active in treating and preventing coccidiosis in poultry (Mrozik, 1974). However, only two examples of 5-amino-1-aryltetrazoles have been structurally characterized to date (Lyakhov *et al.*, 2003). In the present work, we report the crystal structure of a new compound, *viz.* 1-(4-nitrophenyl)-1*H*-tetrazol-5-amine, (I) (Fig. 1).

In our previous investigations of 5-aminotetrazoles (Lyakhov *et al.*, 2001, 2003, 2008), the influence of the conjugation of the 5-amino group lone pair with the π system of the tetrazole ring on the geometric features of the molecules in the crystal structures was studied. It is of interest to investigate similar effects in compounds with other N-containing groups, for example, with the azomethine fragment. For this purpose, we have also investigated {(*E*)-[1-(4-ethoxyphenyl)-1*H*-tetrazol-5-yl]iminomethyl}dimethylamine, (II) (Fig. 2). This compound has practical importance, being useful both as a synthetic intermediate and as a pharmaceutical and agrochemical agent (Tišler, 1983; Granik, 1983; Oshovskii & Pinchuk, 2000), and can be utilized as a tetrazole-containing building block for the synthesis of complex molecules or as a polytopic ligand in bioinorganic, medicinal and supramolecular chemistry. No structural data for tetrazole azomethines are available in the literature.



In both title compounds, the tetrazole ring geometries are similar. The formal double bonds (N2=N3 and N4=C5) are

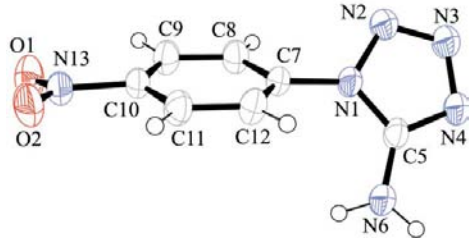


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

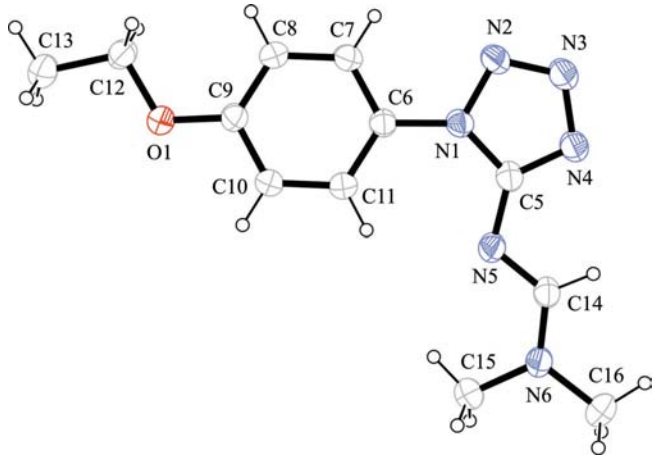


Figure 2
The asymmetric unit of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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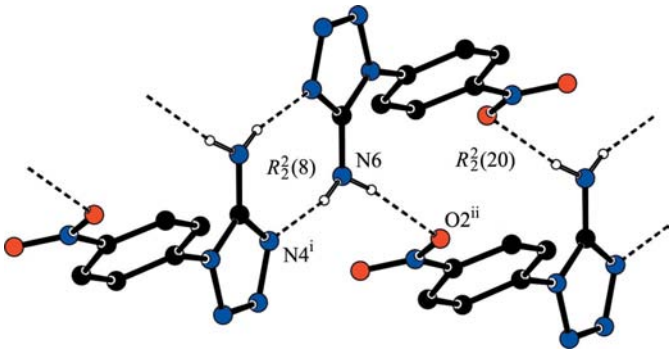

Figure 3
The hydrogen-bonded polymeric chain in (I) running along the [110] direction. Dashed lines indicate hydrogen bonds. Symmetry codes (i) and (ii) correspond to those in Table 2.

the shortest in the ring, while the other three ring bonds lie in a rather narrow range (Tables 1 and 3). The tetrazole rings are essentially planar, with the mean deviations of the tetrazole ring atoms from their least-squares plane being 0.0018 (6) Å for (I) and 0.0013 (10) Å for (II). The geometries of the benzene rings are normal. In (I), the benzene and tetrazole rings are essentially noncoplanar, with a dihedral angle of 54.41 (5)°, while in (II) the corresponding dihedral angle has a rather low value of 4.15 (11)°. This noncoplanarity of the rings in (I) may be caused by steric hindrance due to a 5-amino-group H atom. This assumption agrees with the essential noncoplanarity of the benzene and tetrazole rings in the molecules of all 5-amino-1-aryltetrazoles investigated to date (Lyakhov *et al.*, 2003).

Quantum chemical and X-ray investigations of 5-amino-tetrazoles (Lyakhov *et al.*, 2001, 2003, 2008) show that the conjugation of the 5-amino group lone pair with the π system of the tetrazole ring results in a planar configuration of the amino group, essential shortening of the exocyclic C5—N_{amino} bond and, to a lesser extent, elongation of the C5═N4 tetrazole ring bond. Moreover, the hydrogen bonds formed by the 5-amino group in these crystal structures enhance this effect. For all 5-aminotetrazoles studied to date, the length of the C5—N_{amino} bond lies in the narrow range 1.330 (2)–1.3374 (16) Å (Lyakhov *et al.*, 2001, 2003, 2008; Bray & White, 1979). The data obtained for (I) agree with the above structural peculiarities of 5-aminotetrazoles (Table 1).

Molecules of compound (I) are linked by a combination of N—H···N and N—H···O hydrogen bonds (Table 2), forming polymeric chains running along the [110] direction (Fig. 3). The chain involves two types of centrosymmetric rings with $R_2^2(8)$ and $R_2^2(20)$ motifs (Bernstein *et al.*, 1995) centred at $(\frac{1}{2}+n, n, \frac{1}{2})$ and $(1+n, \frac{1}{2}+n, \frac{1}{2})$, respectively ($n$ = zero or an integer). Only van der Waals interactions are observed between the chains.

The molecule of (II) is essentially flattened, with a mean deviation of the non-H atoms from their least-squares plane of 0.0679 (19) Å. This geometry is favourable for a conjugated system spanning the whole molecule. The same lengths of the formal N5═C14 double and C14—N6 single bonds (Table 3) could be caused by essential conjugation of the N6 atom lone pair with the N5═C14 bond. This conjugation also takes place in solution, as seen in the observed difference in the chemical shifts of signals of formally equivalent *N*-methyl groups in the ^{1}H and ^{13}C NMR spectra. Thus, two singlets of the same intensity were observed in the ^{1}H NMR spectrum (2.99 and 3.16 p.p.m.) and two similar methyl signals were observed in the ^{13}C NMR spectrum (34.3 and 40.4 p.p.m.), which is indicative of the absence of free rotation around the N6—C14 bond in solution. Analysis of the data presented in the Cambridge Structural Database (Version 5.29 of November 2007; Allen, 2002) show that in azomethines with the dialkylamino group at the C atom, the relation between the two bond lengths in the N═C—N fragment is rather different, namely the formal double bond may be shorter, equal to or even longer than the formal single bond, which may be caused by the different influence of the fragments bonded to the azomethine N atom.

In (II), the C5—N5 bond (Table 3) is longer than the C5—N_{amino} bond in 5-aminotetrazoles, which may be an indicative of less conjugation between the lone pair of the azomethine N atom and the tetrazole ring π system in (II) compared with 5-aminotetrazoles. The azomethine fragment is in the *E* configuration. There are no direction-specific interactions between adjacent molecules in (II).

Experimental

1-(4-Nitrophenyl)-1*H*-tetrazol-5-amine, (I), was prepared from 1-(4-nitrophenyl)-1*H*-tetrazole using the one-pot technique reported by Vorobiov *et al.* (2006). Single crystals suitable for X-ray crystal structure analysis were grown by slow evaporation from a tetrahydrofuran–benzene solvent system (2:1 *v*/*v*) at room temperature.

For the preparation of {(*E*)-[1-(4-ethoxyphenyl)-1*H*-tetrazol-5-yl]-iminomethyl}dimethylamine, (II), a solution containing 1-(4-ethoxyphenyl)-1*H*-tetrazol-5-amine (0.01 mol) in methanol (30 ml) was treated with *N*,*N*-dimethylformamide dimethyl acetal (0.02 mol). The reaction mixture was boiled under reflux for 2 h, cooled and kept at 273 K for 10 h. The precipitate which formed was filtered off, washed with cold methanol and dried under reduced pressure (yield 95%, m.p. 421–422 K). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.34 (*t*, 3H, CH_3), 2.99 (*s*, 3H, CH_3), 3.16 (*s*, 3H, CH_3), 4.08 (*q*, 2H, CH_2), 7.08 (*d*, 2H, CH_{Ar}), 7.71 (*d*, 2H, CH_{Ar}), 8.57 (*s*, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.5, 34.3, 40.4, 63.4, 114.8, 124.3, 127.3, 158.2, 158.4, 158.7. Single crystals suitable for X-ray crystal structure analysis were grown by slow evaporation of a benzene solution at room temperature.

Compound (I)

Crystal data

$C_7H_6N_6O_2$
M_r = 206.18
Triclinic, $P\overline{1}$
a = 7.8891 (17) Å
b = 7.9921 (18) Å
c = 8.5877 (18) Å
α = 68.135 (17)°
β = 74.049 (17)°
γ = 63.135 (18)°
V = 444.55 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 295 (2) K
0.48 × 0.44 × 0.42 mm

Table 1
Selected bond lengths (Å) for (I).

N1—C5	1.3516 (12)	N3—N4	1.3617 (13)
N1—N2	1.3722 (12)	N4—C5	1.3269 (12)
N1—C7	1.4223 (11)	N6—C5	1.3376 (13)
N2—N3	1.2794 (12)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H6A···N4^{i}	0.866 (16)	2.119 (17)	2.9684 (14)	166.8 (15)
N6—H6B···O2^{ii}	0.873 (18)	2.234 (18)	3.1003 (14)	171.9 (14)

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

Data collection

Nicolet *R3m* four-circle diffractometer
5556 measured reflections
2605 independent reflections
2338 reflections with $I > 2\sigma(I)$
$R_{int} = 0.011$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.121$
$S = 1.06$
2605 reflections
160 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Compound (II)

Crystal data

$C_{12}H_{16}N_6O$
$M_r = 260.31$
Monoclinic, $P2_1/c$
$a = 8.4150$ (16) Å
$b = 17.514$ (3) Å
$c = 8.8300$ (14) Å
$\beta = 93.694$ (14)°
$V = 1298.7$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 294$ (2) K
0.42 × 0.32 × 0.16 mm

Data collection

Nicolet *R3m* four-circle diffractometer
3232 measured reflections
2999 independent reflections
2132 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.154$
$S = 1.05$
2999 reflections
176 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

In (I), H-atom positions were found from a difference Fourier map and all associated parameters were refined freely. The H atoms in (II) were included in geometrically calculated positions, with C—H = 0.97 Å for the methylene groups, 0.96 Å for the methyl groups and 0.93 Å for the remaining CH groups, and refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups or $1.2U_{eq}(C)$ for all others.

Table 3
Selected bond lengths (Å) for (II).

N1—C5	1.359 (2)	N4—C5	1.330 (2)
N1—N2	1.3647 (19)	C5—N5	1.360 (2)
N1—C6	1.432 (2)	N5—C14	1.313 (2)
N2—N3	1.292 (2)	C14—N6	1.311 (2)
N3—N4	1.356 (2)		

For both compounds, data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON* and *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3250). Services for accessing these data are described at the back of the journal.

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