Crystal data

$C_{17}H_{27}NO_3$
$M_r = 293.41$
Triclinic
$P\bar{1}$
$a = 9.4850\,(13)$ Å
$b = 11.769\,(2)$ Å
$c = 14.596\,(2)$ Å
$\alpha = 104.889\,(12)°$
$\beta = 96.663\,(12)°$
$\gamma = 90.451\,(9)°$
$V = 1562.8\,(4)$ Å^3
$Z = 4$
$D_x = 1.247$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 213 reflections
$\theta = 3–23°$
$\mu = 0.084$ mm^{-1}
$T = 135$ K
Block
$1.02 \times 0.52 \times 0.24$ mm
Pale yellow

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: numerical, based on six indexed crystal faces (Sheldrick, 1996)
$T_{\min} = 0.930$, $T_{\max} = 0.981$
24 913 measured reflections
7688 independent reflections

7473 reflections with $I > 0$
$R_{\rm int} = 0.051$
$\theta_{\max} = 29.85°$
$h = -11 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 20$
332 standard reflections frequency: 540 min intensity decay: none

Refinement

Refinement on F
$R = 0.056$
$wR = 0.052$
$S = 1.070$
7473 reflections
595 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0009F_o^4]$

$(\Delta/\sigma)_{\max} = 0.015$
$\Delta\rho_{\max} = 0.4322$ e Å^{-3}
$\Delta\rho_{\min} = -0.200$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (direct methods) (Sheldrick, 1996). Program(s) used to refine structure: *LSFM* in *MolEN* (Fair, 1990). Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *CIF* in *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1316). Services for accessing these data are described at the back of the journal.

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4-(1*H*-1,2,4-Triazol-1-yl)phenol†

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Abstract

The secondary structure of the title compound, $C_8H_7N_3O$, consists of O—H···N hydrogen-bonding catemers, similar to those of the parent 1,2,4-triazole, where the molecules are linked by N—H···N bonds. Chains related by translation are linked by C—H(triazole)···O/N interactions to give a tertiary structure of corrugated sheets parallel to the *ac* plane. The quaternary structure is due to C—H(Ph)···O contacts and to the stacking of triazole rings from centrosymmetrically related sheets.

Comment

The solid state chemistry of simple phenols has received much attention due to the great variety of structures they present (Perrin *et al.*, 1987). Similarly, heterocyclic compounds, especially azoles, bearing hydroxyphenyl substituents have been studied for their photophysical properties, for instance by ourselves (Catalán *et al.*, 1992, 1995; Foces-Foces *et al.*, 1998). These compounds are also used as ligands in coordination chemistry (La Monica & Ardizzoia, 1997), and a most

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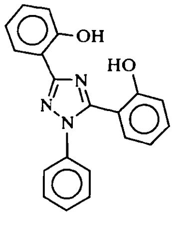
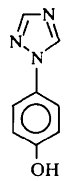
† Alternative name: 1-(4-hydroxyphenyl)-1*H*-1,2,4-triazole.

interesting compound, (I) (Acklin, 1998), shows strong and selective chelation of iron. We report here the solid state structure and properties of 4-(1*H*-1,2,4-triazol-1-yl)phenol, (II).


(I)


(II)

The molecular structure of (II) is shown in Fig. 1. The triazole moiety shows a similar sequence of bond lengths and angles (Table 1) to that found in the parent compound, 1,2,4-triazole (Goldstein *et al.*, 1969; Fuhrmann *et al.*, 1997). However, there are significant differences in the bond distances involving C3 and N4, which may be due to differences in the thermal motion of these atoms in the two structures: the structure of the title compound was determined at 293 K, while the more recent of the two studies of 1,2,4-triazole was carried out at 15 K. The narrower angle at N1 in (II) can be attributed to the electron-donating character of the phenyl ring (Domenicano & Murray-Rust, 1979) The triazole forms a dihedral angle of −31.3 (2)° with the phenyl ring, which is an intermediate value within the range (9.1–80.4°) found for the six other 1-(aryl)-1,2,4-triazole derivatives retrieved from the Cambridge Structural Database (Allen *et al.*, 1991). The rotation of the phenyl ring about the connecting bond to the triazole is sterically hindered if there are substituents in the *ortho* position; thus, the elongation of the connecting bond from 1.405 (15) to 1.431 (2) Å appears to be positively correlated with the N2—N1—C6—C7 dihedral angle (correlation coefficient = 0.857 for the six structures).

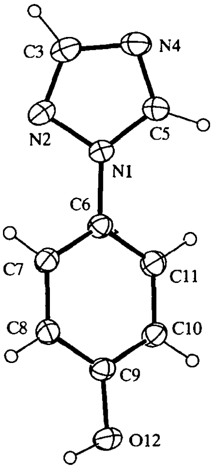
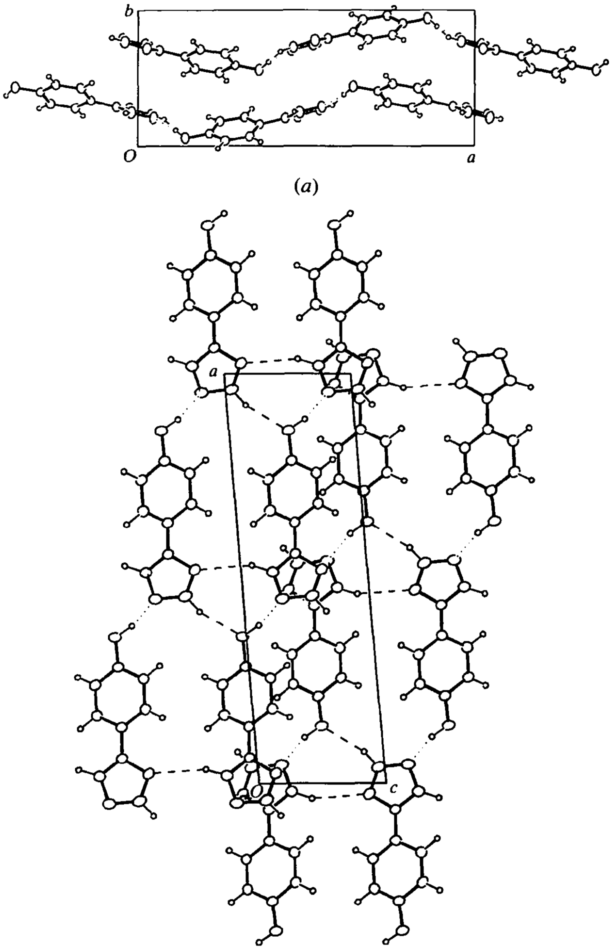


Fig. 1. The molecular structure of (II) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of an arbitrary radius.

The crystal structure of (II) is stabilized by a network of hydrogen bonds (Table 2) between heterochiral catemers running along the *a* axis (Fig. 2*a*). Each catemer is formed by O—H···N contacts linking glide-related molecules. The handedness of the molecules is defined by conformation (the dihedral angle between the triazole and phenyl rings), since the molecule has no chiral centre. Chains related by translation along the *c* axis and joined through the H3 and H5 atoms of the triazole form sheets parallel to the *ac* plane (Fig. 2*b*). Additional stacking of the triazole rings from centrosymmetrically related sheets occurs along the *b* axis to produce a three-dimensional network; tz···tz(1 − *x*, −*y*, 1 − *z*) = 3.686 (1) Å and the perpendicular distance from tz(1 − *x*, −*y*, 1 − *z*) to the triazole plane is 3.451 (1) Å, tz being the centroid of the triazole ring.



(*a*)

(*b*)

Fig. 2. (*a*) A projection along the *c* axis showing the formation of chains in (II) and (*b*) the packing diagram for (II) along the *b* axis, illustrating a pair of sheets related by inversion through ($\frac{1}{2}$,0,$\frac{1}{2}$) and the stacking of the triazoles; dotted and dashed lines represent O—H···N and C—H···N/O hydrogen bonds, respectively.

From the present analysis, the hydroxyphenyl group attached to the N1 atom of the triazole moiety (Fig. 1) does not affect the formation of catemeric hydrogen bonds, which also results in chains in the parent 1,2,4-triazole where molecules related by glide planes are joined by N1—H1···N4 hydrogen bonds. Furthermore, in 1,2,4-triazole, C5—H5···N2 contacts of similar strength to those of the title compound (Table 2) occur between molecules related by 2_1 screw axes, rather than by translation, and link chains to form extended two-dimensional sheets.

Experimental

4-(1*H*-1,2,4-Triazol-1-yl)phenol was prepared by refluxing 4-bromoanisole and 1,2,4-triazole in nitrobenzene in the presence of K_2CO_3 and CuBr, followed by demethylation of the crude intermediate 4-(1,2,4-triazol-1-yl)anisole with 48% HBr, according to the procedure described by Jones *et al.* (1978). The compound melts at 528 K (determined by differential scanning calorimetry, heating rate 2 K min^{-1}) compared with the range of 489–493 K given by Jones *et al.* (1978).

Crystal data

$C_8H_7N_3O$
$M_r = 161.163$
Monoclinic
$P2_1/n$
$a = 18.409$ (2) Å
$b = 7.2898$ (6) Å
$c = 5.6649$ (4) Å
$\beta = 94.96$ (1)°
$V = 757.4$ (1) Å^3
$Z = 4$
$D_x = 1.413$ Mg m^{-3}
D_m not measured
Cu *Kα* radiation
$\lambda = 1.5418$ Å
Cell parameters from 44 reflections
$\theta = 2$–45°
$\mu = 0.817$ mm^{-1}
$T = 293$ K
Rectangular prism
0.33 × 0.17 × 0.10 mm
Colourless

Data collection

Seifert XRD 3000-S diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1657 measured reflections
1324 independent reflections
1104 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.01$
$\theta_{\rm max} = 67.47°$
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 8$
$l = -6 \rightarrow 6$
2 standard reflections
frequency: 100 min
intensity decay: none

Refinement

Refinement on F
$R = 0.051$
$wR = 0.039$
$S = 0.895$
1104 reflections
138 parameters
All H-atom parameters refined
$w = k/[(A + BF_o)^2(C + D\sin\theta/\lambda)]$
$(\Delta/\sigma)_{\rm max} = 0.006$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 5.7 (3) × 10^2
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

N1—N2	1.365 (2)	C3—N4	1.350 (3)
N1—C5	1.331 (2)	N4—C5	1.316 (3)
N1—C6	1.431 (2)	C9—O12	1.364 (2)
N2—C3	1.314 (2)		
N2—N1—C5	109.2 (1)	C3—N4—C5	102.7 (2)
N2—N1—C6	121.9 (1)	N1—C5—N4	110.8 (2)
C5—N1—C6	128.8 (2)	C7—C6—C11	120.7 (2)
N1—N2—C3	102.3 (2)	C8—C9—C10	119.7 (2)
N2—C3—N4	115.1 (2)		
N2—N1—C6—C7	−31.3 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H12···N4$^{\rm i}$	1.00 (3)	1.72 (3)	2.704 (2)	166 (3)
C5—H5···N2$^{\rm ii}$	0.97 (2)	2.58 (2)	3.489 (3)	157 (2)
C3—H3···O12$^{\rm iii}$	0.97 (2)	2.44 (2)	3.373 (3)	161 (2)
C7—H7···O12$^{\rm iv}$	0.97 (2)	2.58 (2)	3.455 (2)	151 (2)

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

Data were recorded at room temperature and the structure was solved by direct methods. The weighting scheme was established empirically so as to give no trends in $<w\Delta^2F>$ *versus* $<F_o>$ or $<\sin\theta/\lambda>$: $w = k/[(A + BF_o)^2(C + D\sin\theta/\lambda)]$. The *A*, *B*, *C* and *D* parameters were adjusted to flatten the initial trends (*PESOS*; Martínez-Ripoll & Cano, 1975). The apparently low ratio of reflections to parameters of 8.00 arises because all H atoms were refined freely.

Data collection: *CRYSOM* (Seifert, 1996). Cell refinement: *LSUCRE* (Appleman, 1994). Data reduction: *Xtal*3.2 (Hall *et al.*, 1992). Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997). Program(s) used to refine structure: *Xtal*3.2. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1323). Services for accessing these data are described at the back of the journal.

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(2-Hydroxyethyl)diisopropylammonium chloride and its derivatives

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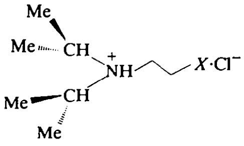
Abstract

The crystal structure of the title compound, $C_8H_{20}NO^+\cdot Cl^-$, (I), and the structures of its derivatives, (2-chloroethyl)diisopropylammonium chloride, $C_8H_{19}ClN^+\cdot Cl^-$, (II), and diisopropyl(2-mercaptoethyl)ammonium chloride, $C_8H_{20}NS^+\cdot Cl^-$, (III), are described. The conformations of the isopropyl groups in (II) (*gauche–gauche*) are different from those in (I) and (III) (both *gauche–trans*). The structures are stabilized by hydrogen bonds of the type Y—H···Cl (Y = N, O, S) and C—H···X (X = Cl, S).

Comment

Crystallographic evidence for the existence of C—H···X (X = O, N, S, Cl) hydrogen bonds was postulated in the pioneering work of Taylor & Kennard (1982). The importance of this type of hydrogen bonding is now well established in crystal engineering and in the supramolecular architectures of organic species, as well as in biomolecular structures and transition metal complexes (Desiraju, 1989, 1996; Jeffrey, 1997; Braga & Grepioni, 1997). Such weak interactions not only play a part in crystal packing, but also have an important role in determining the crystal conformations of flexible molecules (Desiraju, 1989). Recently, the existence of C—H···Cl hydrogen bonding has been described in the crystal structure of triisopropylammonium chloride and it is regarded as being responsible for the conformations of the isopropyl groups on the N atom (Bock *et al.*, 1994).

As part of an on-going study to investigate the electronic and steric effects on the coordination chemistry of *N*-alkylated aminoethanols and the corresponding thiols with Co, Ni and Cu, we prepared (2-hydroxyethyl)diisopropylammonium chloride, (I), (2-chloroethyl)diisopropylammonium chloride, (II), and diisopropyl(2-mercaptoethyl)ammonium chloride, (III). The relationship between the structure and reactivity of these molecules when bulky and rigid groups are incorporated in the main skeleton of the ligands is of interest.



(I) X = OH
(II) X = Cl
(III) X = SH

The molecular structure of (I) is shown in Fig. 1. The O atom is almost *trans* with respect to the N atom and the corresponding N1—C2—C1—O1 torsion angle is 171.9 (2)°. The isopropyl groups on the N atom are arranged in such a way that the H6—C6—N1—H1 and H3—C3—N1—H1 torsion angles are −67.7 and −176.8°, respectively. Thus, H6 is *gauche* and H3 is *trans* (eclipsed) with respect to the ammonium H1 atom. The crystal packing and hydrogen-bonding

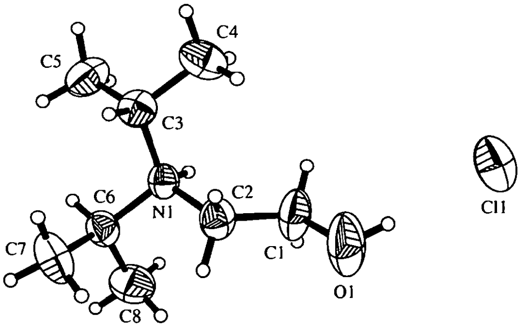


Fig. 1. The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as spheres of an arbitrary radius.

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