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3-Amino-1,2,4-triazine

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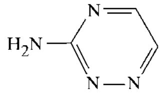
In the crystal structure of 3-amino-1,2,4-triazine, $C_3H_4N_4$, the molecules form hydrogen-bonded chains that are almost parallel to the *b* axis (3.2°), and which are inclined to the *a* and *c* axes by ~21 and ~69°, respectively. The distortion of the 1,2,4-triazine ring in the crystal is compared with gas-phase *ab initio* molecular-orbital calculations.

Comment

The present study is a continuation of our investigation of the characterization of the hydrogen bonds formed by triazine derivatives in the solid state (Janczak & Kubiak, 1999; Janczak & Perpétuo, 2001*a*,*b*,*c*,*d*, 2002; Perpétuo & Janczak, 2002). Triazine and its derivatives, as well as its organic and inorganic complexes or salts, can, *via* multiple hydrogen bonds, develop supramolecular structures by self-assembly of components which contain complementary arrays of hydrogen-bonding sites (Mathias *et al.*, 1994; Zerkowski & Whitesides, 1994; MacDonald & Whitesides, 1994; Row, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). In order to expand the understanding of the solid-state physical–organic chemistry of compounds containing multiple and different hydrogen-bonding systems, we have studied the solid-state structure of 3-amino-1,2,4-triazine, (I). Additionally, the geometry of the molecule has been compared with the *ab initio* fully optimized geometry calculated at the HF/6-31G(*d*,*p*) level (Frisch *et al.*, 1995), and these results are presented here. The *ab initio* molecular-orbital calculations was carried out on the isolated and non-interacting molecule.

The planar six-membered aromatic ring of (I) (Fig. 1) is significantly distorted from the ideal hexagonal form, with the internal C3—N4—C5 angle significantly smaller than 120°. This is a result of the steric effect of a lone-pair electron, predicted by the valence-shell electron-pair repulsion theory (VSEPR; Gillespie, 1963, 1992). Although the other two ring N atoms also have a lone-pair electron, the C6—N1—N2 and C3—N2—N1 angles are less distorted from 120° than the angle containing only one N atom (C3—N4—C5). This is undoubtedly due to the direct bond between the two N atoms (N1—N2), which partially reduces the steric effect of the lone-pair electrons. Additionally, the steric effect of the lone-pair electrons on the N1 and N2 ring atoms is reduced due to hydrogen bonds, in which both ring N atoms are involved as acceptors (Fig. 2).



(I)

The *ab initio* optimized geometry calculated for (I) (Fig. 3) shows a similar correlation between the C—N—C, N—C—N, N—N—C and N—C—C angles within the ring to that found in the crystal. Thus, the ring distortion results mainly from the steric effect of the lone-pair electrons on the ring N atoms and, to a lesser degree, from the hydrogen-bonding system and crystal packing. The values of the N—N, N—C and C—C bond lengths within the 1,2,4-triazine ring in the crystal are comparable with those found in the crystals of other *N*-heteroaromatic derivatives (Allen *et al.*, 1987), but are slightly longer than those in the optimized gas-phase molecule, while the C—NH_2 bond is longer in the optimized molecule than in the crystal.

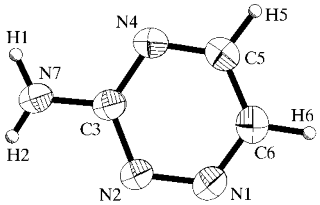


Figure 1
A view of the molecule of (I), drawn with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

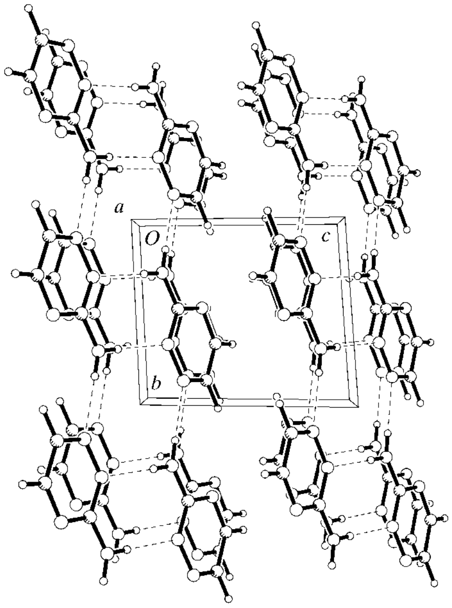


Figure 2
A projection of the structure of (I) along [100], showing molecules connected into chains by N—H···N interactions.

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In the crystal structure of (I) (Fig. 2), the molecules are parallel to each other. Each 3-amino-1,2,4-triazine molecule is involved in four hydrogen bonds, in two as a donor and in the other two as an acceptor. The hydrogen-bonded molecules form chains that are almost parallel to the *b* axis (3.2°), and which are inclined by ~21 and ~69° to the *a* and *c* axes, respectively. The chains of hydrogen-bonded molecules are parallel to each other, forming a stacking structure. Within one stack, the molecules are separated by a distance of ~2.88 Å. This distance is significantly shorter than the distance between the π-aromatic ring systems (Pauling, 1960) and indicates a strong π–π interaction between the 1,2,4-triazine rings within the stacks (Fig. 2).

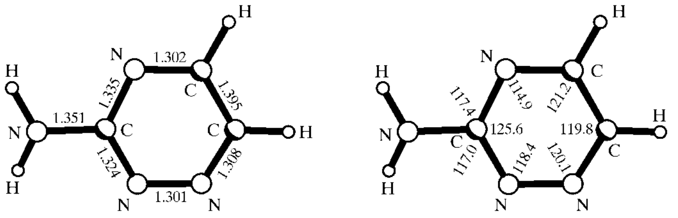

Figure 3
The results of the optimized gas-phase calculations on 3-amino-1,2,4-triazine. Bond lengths are given in Å and angles in °.

Experimental

Crystals of (I) were obtained by sublimation under vacuum and using a temperature gradient. The powder of 3-amino-1,2,4-triazine was placed in an evacuated glass ampoule (*ca* 25 ml) and the ampoule placed in the temperature gradient. Crystals of (I) appeared in the cooler part of the glass ampoule.

Crystal data

$C_3H_4N_4$
M_r = 96.10
Triclinic, $P\overline{1}$
a = 5.225 (1) Å
b = 6.166 (1) Å
c = 7.079 (1) Å
α = 84.03 (3)°
β = 76.88 (3)°
γ = 77.81 (3)°
V = 216.73 (7) Å^3
Z = 2
D_x = 1.473 Mg m^{-3}
D_m = 1.47 Mg m^{-3}
D_m measured by flotation in dibromoethane/chloroform
Mo $K\alpha$ radiation
Cell parameters from 28 reflections
θ = 8–14°
μ = 0.11 mm^{-1}
T = 295 (2) K
Parallelepiped, light yellow
0.34 × 0.22 × 0.18 mm

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical face-indexed (*SHELXTL*; Sheldrick, 1990)
$T_{\min}$ = 0.972, $T_{\max}$ = 0.981
2005 measured reflections
1021 independent reflections
668 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.013
$\theta_{\max}$ = 28.2°
$h = -6 \rightarrow 6$
$k = -6 \rightarrow 8$
$l = -9 \rightarrow 9$
2 standard reflections every 50 reflections intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.083
S = 1.01
1021 reflections
81 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 0.0537P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 0.18 e Å^{-3}
$\Delta\rho_{\min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.061 (12)

Table 1
Selected geometric parameters (Å, °).

N1—C6	1.316 (2)	C3—N7	1.330 (2)
N1—N2	1.336 (2)	C3—N4	1.351 (2)
N2—C3	1.357 (2)	N4—C5	1.311 (2)
C6—N1—N2	119.1 (1)	N4—C3—N2	124.9 (1)
N1—N2—C3	118.1 (1)	C5—N4—C3	115.0 (1)
N7—C3—N4	118.6 (1)	N4—C5—C6	121.8 (1)
N7—C3—N2	116.4 (1)	N1—C6—C5	121.0 (1)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H1···N1$^{\rm i}$	0.88 (2)	2.13 (2)	3.013 (2)	178 (2)
N7—H2···N2$^{\rm ii}$	0.84 (2)	2.21 (2)	3.054 (2)	178 (2)

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

The refined C—H distances are 0.98 (12) and 1.04 (2) Å

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1577). Services for accessing these data are described at the back of the journal.

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