

## 2-*tert*-Butylamino-4-chloro-6-ethylamino-1,3,5-triazine: a structure with $Z' = 4$ containing two different molecular conformations and two independent chains of hydrogen-bonded $R_2^2(8)$ rings

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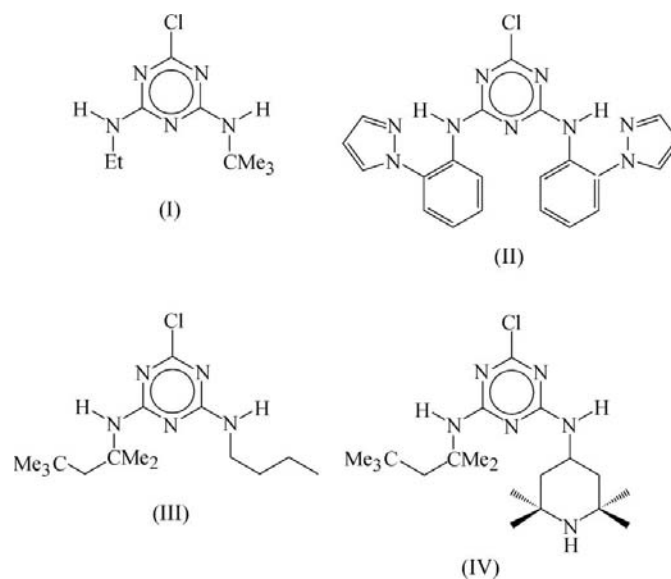
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The title compound (trivial name *tert*butylazine),  $C_9H_{16}ClN_5$ , (I), crystallizes with  $Z' = 4$  in the space group  $Pca2_1$ , and equal numbers of molecules adopt two different conformations for the ethylamine groups. The four independent molecules form two approximately enantiomorphic pairs. Eight independent  $N-H \cdots N$  hydrogen bonds link the molecules into two independent chains of  $R_2^2(8)$  rings, in which the arrangement of the alkylamine substituents in the independent molecules precludes any further crystallographic symmetry. The significance of this study lies in its finding of two distinct molecular conformations within the structure and two distinct ways in which the molecules are organized into hydrogen-bonded chains, and in its comparison of the hydrogen-bonded structure of (I) with those of analogous 1,3,5-triazines and pyrimidines.

### Comment

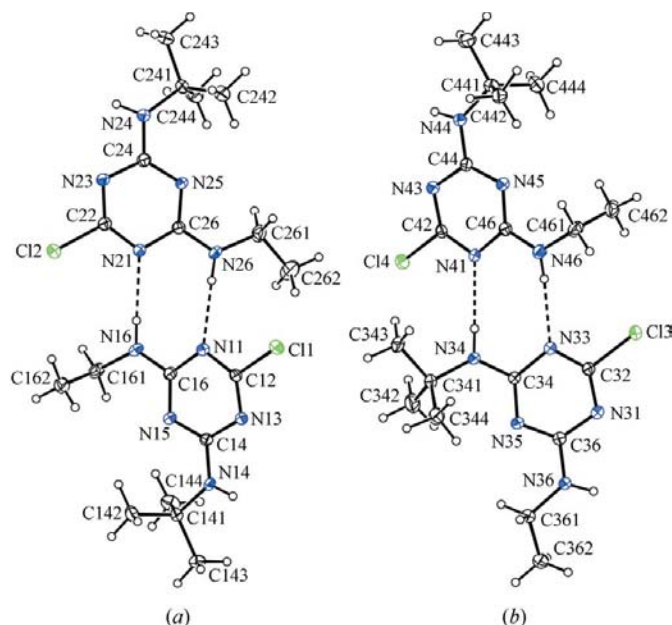
The formation of hydrogen-bonded rings of type  $R_2^2(8)$  (Bernstein *et al.*, 1995) built from pairs of  $N-H \cdots N$  hydrogen bonds is a very common motif in the structures of aminopyrimidines which readily leads to the formation of chains of these rings (Rodríguez *et al.*, 2008). We have recently attempted a rationalization of the patterns of supramolecular aggregation in 4,6-disubstituted 2-aminopyrimidines in terms of the formation *versus* fragmentation of such chains (Rodríguez *et al.*, 2008). The formation of continuous chains of  $R_2^2(8)$  rings can, in fact, be disrupted either by steric factors asso-

ciated with bulky substituents or by the presence of alternative hydrogen-bond acceptors, giving in some cases short-chain fragments containing only four molecules, and in other cases only isolated dimer units. A number of the examples considered in the earlier study contain one chlorine substituent and two amine substituents, usually different, on the pyrimidine ring. With this in mind, we have now extended our study to encompass a similarly substituted 1,3,5-triazine derivative, the title compound, (I) (Fig. 1), the structure of which we report here along with a comparative analysis of the related structures (II)–(IV) retrieved from the Cambridge Structural Database (CSD, Version of December 2007; Allen, 2002).



Compound (I) crystallizes with  $Z' = 4$  in the space group  $Pca2_1$ , and the selected asymmetric unit consists of two hydrogen-bonded aggregates (Table 1). Molecules 1 and 2, containing atoms N11 and N21, respectively, are linked by two  $N-H \cdots N$  hydrogen bonds in which the ethylamine atoms N16 and N26 act as the donors, forming an  $R_2^2(8)$  ring. We denote this aggregate dimer *A* (Fig. 1*a*). By contrast, in dimer *B*, formed by molecules 3 and 4 (containing atoms N31 and N41, respectively), the hydrogen-bond donors in the  $R_2^2(8)$  ring are atoms N34 and N46, which are parts of a *tert*-butylamine and an ethylamine group, respectively (Fig. 1*b*). Hence, in dimer *A* the two independent *tert*-butylamine groups are *trans* to one another in the dimer, whereas in dimer *B* the *tert*-butylamine group based on atom N44 is *trans* to the ethylamine group based on atom N36. Possibly the simplest way to envisage the relationship between dimers *A* and *B* is *via* a  $180^\circ$  rotation of molecule 3 about the line  $Cl3-C32 \cdots N35$ .

The different arrangements of the alkylamine substituents in the two dimers are sufficient to preclude the possibility of any additional crystallographic symmetry. In addition, the conformations of the ethylamine groups differ (Table 2), although those of the *tert*-butylamine groups are all fairly similar. The  $C-N-C-C$  torsion angles defining the orientation of the ethyl groups indicate that the conformations of molecules 1 and 4 are similar, although approximately enantiomorphic, as are those of molecules 2 and 3, which are



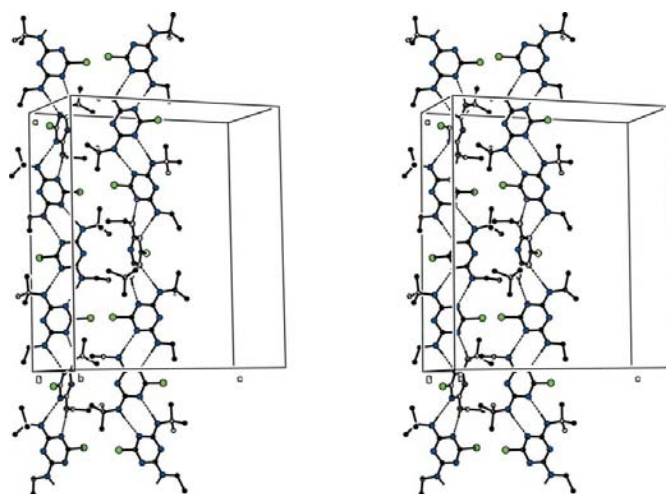
**Figure 1**

The independent molecular components in compound (I), showing the atom-labelling scheme and the two hydrogen-bonded dimers formed within the selected asymmetric unit. (a) Dimer A formed from molecules 1 and 2, and (b) dimer B formed from molecules 3 and 4. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines.

also approximately enantiomorphic. In each of the independent molecules, the alkylamine substituents are oriented so that the  $N_{x4}-C_{x41}$  and  $N_{x6}-C_{x61}$  bonds (where  $x = 1-4$ ) are all approximately parallel to the corresponding  $C_{x2}-Cl_x$  bonds (Table 2). It is interesting to note that the  $C_{x41}$  atoms in the *tert*-butyl groups ( $x = 1-4$ ) and the  $C_{x61}$  atoms in the ethyl groups ( $x = 1-4$ ) do not deviate greatly from the planes of the adjacent triazine rings, as shown by the key torsion angles (Table 2).

In addition to the hydrogen bonds within the two independent dimers, there are four further  $N-H \cdots N$  hydrogen bonds which link these dimers into chains (Table 1). In the type A dimer, atoms N14 and N24 at  $(x, y, z)$  act as hydrogen-bond donors to, respectively, N23 at  $(-\frac{1}{2} + x, 1 - y, z)$  and N13 at  $(\frac{1}{2} + x, 1 - y, z)$ , so forming a  $C_2^2(10)C_2^2(10)[R_2^2(8)][R_2^2(8)]$  chain of rings consisting of type A dimers related by the  $c$ -glide plane at  $y = \frac{1}{2}$  (Fig. 2). The final two  $N-H \cdots N$  hydrogen bonds, having atoms N31 and N43 as the acceptors, give rise to an entirely analogous chain of type B dimers related by the  $c$ -glide plane at  $y = 0$  (Fig. 2). There are two chains of each type passing through each unit cell, but there are no direction-specific interactions between the chains. In particular, there are no  $C-H \cdots \pi(\text{triazine})$  hydrogen bonds and no  $\pi-\pi$  stacking interactions in the structure.

The structures of three related compounds, (II)–(IV) (see scheme), each bearing one chlorine substituent and two primary amine substituents on a single 1,3,5-triazine ring, are recorded in the CSD. The original reports on these structures all essentially presented proof of constitution, with no analysis or discussion of the supramolecular aggregation, and it is

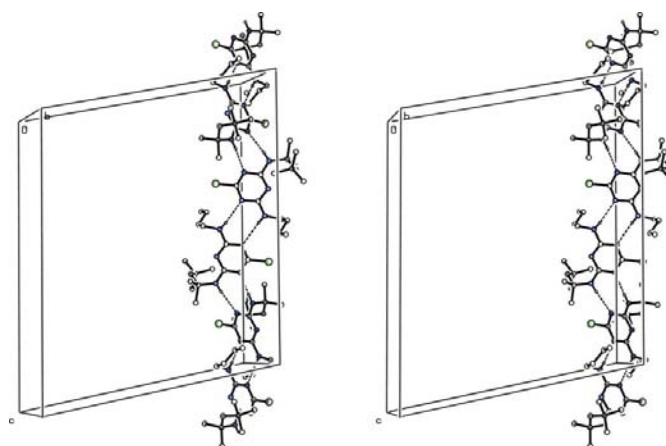


**Figure 2**

A stereoview of part of the crystal structure of (I), showing the formation of the two independent hydrogen-bonded chains of rings. For the sake of clarity, H atoms bonded to C atoms have all been omitted. Hydrogen bonds are indicated by dashed lines.

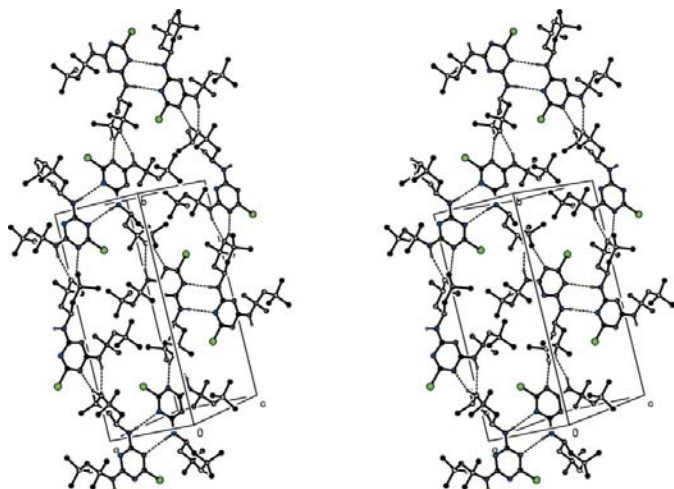
therefore of interest briefly to compare their structures with that of compound (I). In each case, the hydrocarbyl fragments in the alkylamine substituents are oriented with the  $N-C$  bonds approximately parallel to the  $C-Cl$  bond, as in compound (I). Hence, the ring atom N5 is never available as a potential hydrogen-bond acceptor. In compound (II) (CSD refcode EQOMEC; Diaz-Ortiz *et al.*, 2003), there are two intramolecular  $N-H \cdots N$  hydrogen bonds forming  $S(6)$  rings, but there are no direction-specific interactions between the molecules.

There are two intermolecular  $N-H \cdots N$  hydrogen bonds in compound (III) (CSD refcode UFAGUE; Wen *et al.*, 2007), and the authors commented only that the hydrogen bonds form a zigzag chain along [001]. In fact, one of the hydrogen



**Figure 3**

A stereoview of part of the crystal structure of (III) (CSD refcode UFAGUE; Wen *et al.*, 2007), showing the formation of a hydrogen-bonded chain along [001] containing two independent  $R_2^2(8)$  rings. The original atom coordinates have been used (Wen *et al.*, 2007). For the sake of clarity, H atoms bonded to C atoms have all been omitted. Hydrogen bonds are indicated by dashed lines.



**Figure 4**

A stereoview of part of the crystal structure of (IV) (CSD refcode SILTEN; Dong & Huang, 2007), showing the formation of a hydrogen-bonded sheet parallel to (101) containing rings of  $R_2^2(6)$ ,  $R_2^2(8)$  and  $R_6^0(40)$  types. The original atom coordinates have been used (Dong & Huang, 2007). For the sake of clarity, H atoms bonded to C atoms have all been omitted. Hydrogen bonds are indicated by dashed lines.

bonds links pairs of molecules related by inversion, forming the familiar  $R_2^2(8)$  ring motif, while the other links pairs of molecules related by rotation about a twofold axis in the space group  $C2/c$ , so forming a second, independent,  $R_2^2(8)$  motif. The combination of these two motifs thus generates a chain of  $R_2^2(8)$  rings along [001] (Fig. 3). Two chains of this type, related to one another by the  $C$ -centring operation, pass through each unit cell, but with no direction-specific interactions between adjacent chains.

The structure of compound (IV) (CSD refcode SILTEN; Dong & Huang, 2007) was described by the authors in terms of chains along [010], although three independent intermolecular  $N-H\cdots N$  hydrogen bonds were recorded. Re-examination of this structure shows, in fact, that the molecules are linked into sheets. One of the hydrogen bonds links inversion-related pairs of molecules to form the usual  $R_2^2(8)$  dimers, and these units are further linked by the other two hydrogen bonds to form sheets parallel to (101) containing three types of ring, *viz.* of  $R_2^2(6)$ ,  $R_2^2(8)$  and  $R_6^0(40)$  types (Fig. 4). The formation of the large  $R_6^0(40)$  rings in compound (IV) is probably controlled and effectively templated by the pair of inversion-related  $-CMe_2CH_2CMe_3$  substituents within it (Fig. 4).

As in the pyrimidine series discussed recently (Rodríguez *et al.*, 2008), so too in the analogous 1,3,5-triazines, where alternative hydrogen-bond acceptors are absent and the steric requirements of the substituents are not extreme, chains of  $R_2^2(8)$  rings are formed, as in compounds (I) and (III). However, where alternative hydrogen-bond acceptors are available, the chain of rings can readily be disrupted, as in compound (IV), where the  $R_2^2(8)$  dimer unit which forms the basic building block for the sheet formation provides the sole trace of any chain of rings, and in compound (II), where the intramolecular hydrogen bonding effectively prevents any intermolecular hydrogen-bond formation.

## Experimental

A sample of compound (I) was purchased from Riedel de Haën. Crystals suitable for single-crystal X-ray diffraction (m.p. 449 K) were obtained by slow evaporation of a solution in ethanol–water (1:1 *v/v*).

### Crystal data

$C_9H_{16}ClN_5$	$V = 4785.9 (10) \text{ \AA}^3$
$M_r = 229.72$	$Z = 16$
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation
$a = 23.557 (3) \text{ \AA}$	$\mu = 0.30 \text{ mm}^{-1}$
$b = 9.9789 (15) \text{ \AA}$	$T = 120 (2) \text{ K}$
$c = 20.3594 (17) \text{ \AA}$	$0.45 \times 0.30 \times 0.25 \text{ mm}$

### Data collection

Bruker–Nonius KappaCCD diffractometer	113172 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	10971 independent reflections
$T_{\min} = 0.878$ , $T_{\max} = 0.929$	7899 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.070$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$	H-atom parameters constrained
$wR(F^2) = 0.160$	$\Delta\rho_{\text{max}} = 1.29 \text{ e \AA}^{-3}$
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$
10971 reflections	Absolute structure: Flack (1983),
557 parameters	with 5308 Friedel pairs
1 restraint	Flack parameter: 0.11 (6)

**Table 1**

Hydrogen-bond geometry for compound (I) ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N14-H14\cdots N23^i$	0.88	2.24	3.118 (4)	173
$N16-H16\cdots N21$	0.88	2.17	3.049 (4)	175
$N24-H24\cdots N13^{ii}$	0.88	2.21	3.090 (4)	175
$N26-H26\cdots N11$	0.88	2.14	3.019 (4)	179
$N34-H34\cdots N41$	0.88	2.22	3.093 (4)	172
$N36-H36\cdots N43^{iii}$	0.88	2.16	3.039 (4)	175
$N44-H44\cdots N31^{iv}$	0.88	2.36	3.228 (4)	170
$N46-H46\cdots N33$	0.88	2.14	3.020 (4)	174

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

**Table 2**

Selected torsion angles ( $^\circ$ ) for compound (I).

	$x = 1$	$x = 2$	$x = 3$	$x = 4$
$Nx1-Cx6-Nx6-Cx61$	-174.6 (3)	173.8 (4)	-179.8 (4)	179.3 (3)
$Cx6-Nx6-Cx61-Cx62$	82.5 (4)	-163.5 (4)	163.5 (4)	-80.7 (5)
$Nx3-Cx4-Nx4-Cx41$	179.9 (3)	-176.8 (4)	-173.2 (3)	-176.5 (3)
$Cx4-Nx4-Cx41-Cx42$	-64.8 (5)	-58.3 (5)	-72.0 (5)	-58.9 (5)
$Cx4-Nx4-Cx41-Cx43$	178.3 (4)	-174.4 (4)	169.9 (4)	-176.9 (4)
$Cx4-Nx4-Cx41-Cx44$	60.1 (5)	67.4 (5)	51.9 (5)	64.6 (5)

The systematic absences permitted  $Pca2_1$  and  $Pcam$  (=  $Pbcm$ , No. 57) as possible space groups.  $Pca2_1$  was selected and confirmed by the subsequent structure analysis. Although the ADDSYM routine in PLATON (Spek, 2003) suggested possible inversion symmetry in the space group  $Pbca$ , the molecular conformations and the pattern of the intermolecular hydrogen bonds both preclude any additional crystallographic symmetry.

All H atoms were located in difference maps and treated as riding atoms in geometrically idealized positions, with  $C-H = 0.98$  ( $CH_3$ ) or  $0.99 \text{ \AA}$  ( $CH_2$ ) and  $N-H = 0.86 \text{ \AA}$ , and with  $U_{\text{iso}}(H) = kU_{\text{eq}}(\text{parent})$ ,

where  $k = 1.5$  for the methyl groups and 1.2 for all other H atoms. The two maxima in the final difference map are located 1.46 Å from atom Cl3 ( $1.29 \text{ e } \text{Å}^{-3}$ ) and 1.43 Å from atom Cl2 ( $1.19 \text{ e } \text{Å}^{-3}$ ). The correct orientation of the structure with respect to the polar-axis direction was established using the Flack parameter (Flack, 1983).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALLCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3255). Services for accessing these data are described at the back of the journal.

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