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Hydrogen-bonding patterns in two structural isomers of 3,6-bis(2-chlorophenyl)-1,4-dihydro-1,2,4,5-tetrazine

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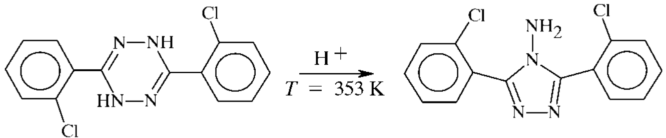
Two structural isomers, 3,6-bis(2-chlorophenyl)-1,4-dihydro-1,2,4,5-tetrazine, (I), and 3,5-bis(2-chlorophenyl)-4-amino-1*H*-1,2,4-triazole, (II), both $C_{14}H_{10}Cl_2N_4$, form chain-like structures in the solid state, stabilized by N—H···N and N—H···Cl hydrogen bonds. A contribution from weak interactions to the strong hydrogen-bond network is observed in both structures. The secondary graph sets for intermolecular hydrogen bonds [$R_2^2(11)$ for (I) and $R_2^2(12)$ for (II)] indicate the similarity between the networks.

Comment

The compound of general formula $C_2H_2N_4(C_6H_4Cl)_2$ crystallizes as 3,6-bis(2-chlorophenyl)-1,4-dihydro-1,2,4,5-tetrazine, (I), in the form of yellow–orange needles. It undergoes irreversible isomerization above 353 K in acidic water solution, forming the structural isomer 3,5-bis(2-chlorophenyl)-4-amino-1*H*-1,2,4-triazole, (II).



(I) (II)

X-ray structure determination revealed that isomer (I) crystallizes in the monoclinic space group *C*2/*c*, while isomer (II) crystallizes in the orthorhombic space group *Pbca*. The molecular structures of (I) and (II), with the atom-numbering schemes, are shown in Figs. 1 and 2, respectively, and selected geometric parameters are given in Tables 1 and 3.

Since both molecules retain potential strong proton-donor groups [–NH in (I) and –NH_2 in (II)] and proton acceptors (N and Cl atoms), we undertook a detailed analysis of the hydrogen-bonded networks. Analysis of intra- and intermolecular contacts occurring in crystalline isomers indicated that, in both cases, the weaker C—H donor groups are also important in the formation of the hydrogen-bonded network (Taylor & Kennard, 1982; Desiraju & Steiner, 1999). To attempt a consistent characterization of the differences and similarities of the solid-state structures of the studied compounds, we have used the Etter (1990, 1991) graph-set descriptors.

The molecule of (I) consists of a six-membered central tetrazine ring and two chlorophenyl rings. As a twofold axis passes through the centre of the tetrazine ring, the molecule exhibits crystallographic C_2 point-group symmetry, so the chlorophenyl rings are symmetry equivalent. The central ring is folded along the N1···N1^i vector [symmetry code: (i) $-x, y, \frac{1}{2} - z$] and exhibits a boat conformation [puckering parameters $Q = 0.513$ (2)°, $\theta = 90.0$ (2)° and $\varphi = 175.7$ (2)°; Cremer & Pople, 1975]. An analysis of structures deposited in the Cambridge Structural Database (Version 5.24 of April 2003; Allen, 2002) showed that a boat conformation is observed for all structurally characterized tetrazine derivatives. The chlorophenyl rings are twisted towards one another with a dihedral angle of 77.94 (7)°. The Cl atoms lie on the same side of the C10/N2/C10^i/N2^i plane. Atoms N1 and N1^i lie above this plane, and atoms H1 and H1^i are located in equatorial positions. Such an arrangement enables the formation of a pair of strong intermolecular N—H···N hydrogen bonds between centrosymmetrically related neighbouring molecules [Table 2; hydrogen-bond motif $R_2^2(6)$ (Bernstein *et al.*, 1995), shown as motif *a* in Fig. 3], leading to the formation of an infinite $C(4)[R_2^2(6)]$ chain of rings along the *c* axis.

The molecule of (II) consists of a five-membered (heterocyclic) aromatic triazole ring and two chlorophenyl rings (Ph1 and Ph2). The main difference from the molecule of (I) is the asymmetry of the molecule of (II), in which the H atoms of the –NH_2 amine group lie on the same side of the quasi-mirror plane that is perpendicular to the ring plane and passes through the amine N atom and the ring N—N bond. Excluding these H atoms, the molecule displays almost C_m point-group

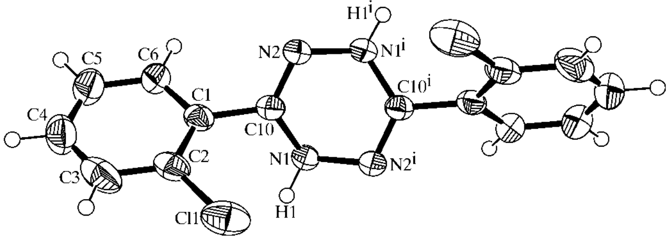


Figure 1
The molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

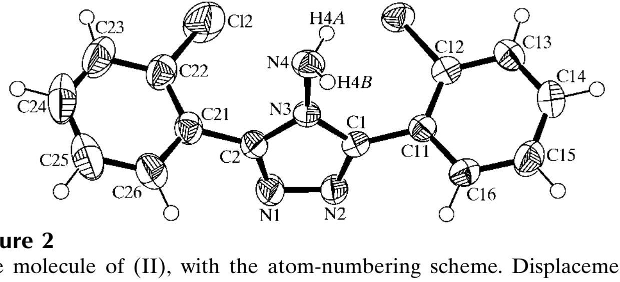


Figure 2
The molecule of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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symmetry. The main reason for the asymmetry of the molecule is the strong N4—H4*B*···N2 intermolecular hydrogen bond (Table 4). An infinite zigzag *C*(5) chain (motif *a* in Fig. 4) is formed by molecules related by a *b*-glide plane. As atoms H4*A* and H4*B* are both directed towards ring Ph1, an intramolecular hydrogen bond is formed between the N4—H4*A* donor group and atom Cl1. The corresponding graph-set descriptor is *S*(7) (motif *b* in Fig. 4). This interaction is also evidenced by the significantly different displacement parameters of atoms Cl1 and Cl2, the U_{eq} values being 0.0503 (2) and 0.0908 (3) Å^2, respectively. The dihedral angles between the triazole plane and the planes of rings Ph1 and Ph2 are 60.06 (7) and 65.21 (8)°, respectively. The larger value for ring Ph2 is a consequence of the repulsion between atoms Cl2 and N4 [Cl2···N4 = 3.378 (3) Å].

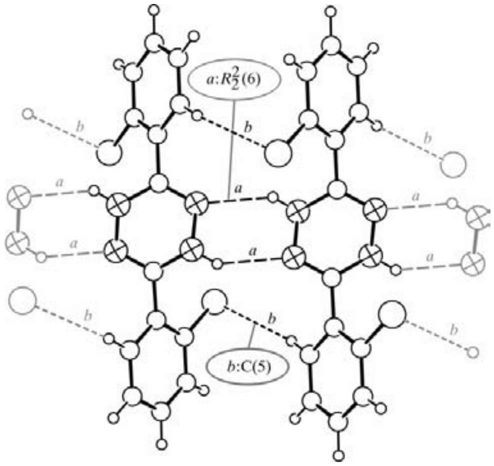

Figure 3
A map of the hydrogen-bond patterns in the main structural feature of (I). Hydrogen bonds are shown as dashed and dotted lines. For motif *a*, a full description of the pattern is $C(4)[R_2^2(6)]$ (Bernstein *et al.*, 1995). The two motifs together constitute the first-order hydrogen-bonded network described as $N1 = C(5)C(4)[R_2^2(6)]$.

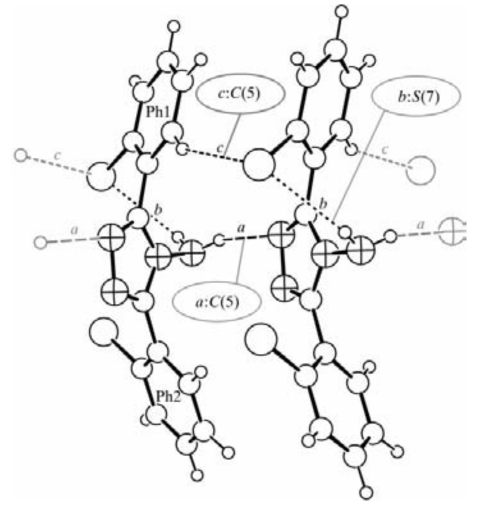

Figure 4
A map of the hydrogen-bond patterns in the main structural feature of (II). Hydrogen bonds are shown as dashed and dotted lines. The three motifs together constitute the first-order hydrogen-bonded network described as $N1 = C(5)S(7)C(5)$.

The one-dimensional assemblies formed by strong hydrogen bonding are enforced by weaker intermolecular interactions. C—H···Cl contacts are observed along the main chains, between the chlorophenyl rings of adjacent molecules. The H···Cl distances [2.83 (3) Å in (I) and 2.85 (2) Å in (II)] are typical of relatively strong C—H···Cl bonding (Taylor & Kennard, 1982). The assigned graph-set descriptors are *C*(5) for both compounds (motif *b* in Fig. 3 and motif *c* in Fig. 4). Motifs *a*, *b* and *c* constitute primary graph sets {$N_1 = C(5)C(4)[R_2^2(6)]$ for (I) and $N_1 = C(5)S(7)C(5)$ for (II); Etter *et al.*, 1990}. The first-level graph sets are different because of the presence of symmetry-equivalent atoms in (I) and intramolecular hydrogen bonding in (II). The secondary graph sets for intermolecular bonding are $N_2(ab) = R_2^2(11)$ [for (I)] and $N_2(ac) = R_2^2(12)$ [for (II)], indicating the similarity of the main structural features in (I) and (II).

Detailed analysis of the molecular packing shows that the main chains form close-packed structures. In the case of (II), the zigzag chains are connected together *via* C24—H24···N4^{v} and C13—H13···N2^{vi} weak hydrogen bonds (Table 4), with motifs $R_2^2(16)$ and *C*(6), respectively. There is no evidence of weak hydrogen bonding between the chains of (I), but by analogy to the crystal structure of (II), the long C3—H3···N1($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$) contact [H···N = 2.98 (3) Å] can be regarded as an attractive interaction. The same graph-set descriptor, *C*(6), is applicable.

Experimental

Compound (I) was prepared using a modification of the procedure described by Brooker *et al.* (1987), by reacting bis(α,2-dichlorobenzylidene)hydrazine and hydrazine hydrate at low temperature. Crystals suitable for X-ray diffraction were crystallized from ethanol, precipitating in the form of yellow–orange needles (m.p. 482–483 K). Compound (I) was dissolved in an acidic water solution and heated to above 353 K, giving the structural isomer (II). The isomerization reaction is irreversible. Well shaped crystals of (II), in the form of colourless prisms (m.p. 441–442 K), were obtained from ethanol. Detailed descriptions of the products and synthesis routes are given elsewhere (Włostowski & Olszewski, 2004).

Isomer (I)

Crystal data

$C_{14}H_{10}Cl_2N_4$
$M_r = 305.16$
Monoclinic, $C2/c$
$a = 16.0020$ (12) Å
$b = 9.4123$ (8) Å
$c = 10.5752$ (7) Å
$\beta = 121.664$ (5)°
$V = 1355.69$ (18) Å^3
$Z = 4$

$D_x = 1.495$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 30 reflections
$\theta = 7.7$–16.4°
$\mu = 0.47$ mm^{-1}
$T = 293$ (2) K
Needle, yellow–orange
0.62 × 0.09 × 0.09 mm

Data collection

Siemens *P*3 diffractometer
ω–2θ scans
Absorption correction: Gaussian (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.936$, $T_{max} = 0.960$
2496 measured reflections
1203 independent reflections
996 reflections with $I > 2\sigma(I)$

$R_{int} = 0.014$
$\theta_{max} = 25.0$°
$h = -18 \rightarrow 18$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$
1 standard reflection every 70 reflections
intensity decay: 1.8%

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.099$
$S = 1.04$
1203 reflections
112 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 1.4393P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.39$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0047 (12)

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

Cl1—C2	1.730 (2)	N1—N2$^{\rm i}$	1.438 (2)
N1—C10	1.398 (2)	N2—C10	1.273 (2)
C10—N1—N2$^{\rm i}$	114.14 (15)	N1—C10—C1	118.55 (16)
C10—N2—N1$^{\rm i}$	111.68 (16)	C1—C2—Cl1	120.20 (17)
N2—C10—N1	121.13 (18)	C3—C2—Cl1	119.56 (19)
N2—C10—C1	120.07 (17)		
N1$^{\rm i}$—N2—C10—N1	1.4 (3)	N2$^{\rm i}$—N1—C10—N2	39.8 (2)
N1$^{\rm i}$—N2—C10—C1	−172.72 (17)	N2$^{\rm i}$—N1—C10—C1	−146.05 (18)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N2$^{\rm ii}$	0.88 (2)	2.29 (2)	3.052 (2)	145 (2)
C6—H6···Cl1$^{\rm iii}$	0.98 (2)	2.83 (2)	3.732 (2)	154 (2)

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

Iosmer (II)

Crystal data

$C_{14}H_{10}Cl_2N_4$
$M_r = 305.16$
Orthorhombic, *Pbca*
$a = 12.3382$ (14) Å
$b = 8.6777$ (9) Å
$c = 25.968$ (4) Å
$V = 2780.3$ (6) Å^3
$Z = 8$
$D_x = 1.458$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 29 reflections
$\theta = 4.1$–$10.3°$
$\mu = 0.46$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.49 × 0.18 × 0.12 mm

Data collection

Siemens *P*3 diffractometer
ω–2θ scans
Absorption correction: Gaussian (*SHELX*76; Sheldrick, 1976)
$T_{\rm min} = 0.913$, $T_{\rm max} = 0.952$
2461 measured reflections
2461 independent reflections
1662 reflections with $I > 2\sigma(I)$
$\theta_{\rm max} = 25.1°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 10$
$l = -30 \rightarrow 0$
2 standard reflections every 70 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.098$
$S = 1.02$
2461 reflections
222 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0016 (4)

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

Cl1—C12	1.743 (2)	N2—C1	1.311 (3)
Cl2—C22	1.725 (3)	N3—C2	1.358 (2)
N1—C2	1.310 (3)	N3—C1	1.361 (3)
N1—N2	1.395 (3)	N3—N4	1.410 (2)
C2—N1—N2	107.30 (18)	N2—C1—C11	126.33 (19)
C1—N2—N1	107.46 (17)	N3—C1—C11	124.31 (18)
C2—N3—C1	106.45 (17)	N1—C2—N3	109.53 (18)
C2—N3—N4	124.73 (17)	N1—C2—C21	125.9 (2)
C1—N3—N4	128.39 (17)	N3—C2—C21	124.55 (19)
N2—C1—N3	109.26 (19)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4*B*···N2$^{\rm iv}$	0.88 (3)	2.19 (3)	3.016 (3)	154 (2)
N4—H4*A*···Cl1	0.83 (3)	2.66 (3)	3.321 (2)	137 (2)
C16—H16···Cl1$^{\rm iv}$	0.98 (2)	2.85 (2)	3.734 (2)	151 (2)
C24—H24···N4$^{\rm v}$	0.96 (3)	2.66 (3)	3.567 (4)	157 (2)
C13—H13···N2$^{\rm vi}$	0.93 (2)	2.69 (2)	3.568 (3)	158 (2)

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

For both compounds, H atoms were found from a difference Fourier map and their positional and isotropic displacement parameters were refined.

For both compounds, data collection: *P*3/*P*4-*PC Software* (Siemens, 1991); cell refinement: *P*3/*P*4-*PC Software*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1670). Services for accessing these data are described at the back of the journal.

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