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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.007 Å
Disorder in main residue
R factor = 0.077
wR factor = 0.187
Data-to-parameter ratio = 15.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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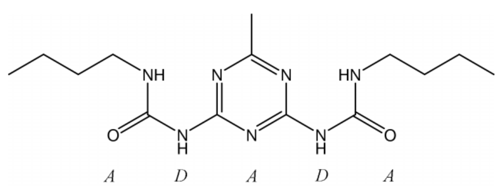
The formation of a quadruply hydrogen-bonded dimer of the title compound, $C_{14}H_{25}N_7O_2$, is prevented by an intramolecular hydrogen bond, which disrupts the linear *ADADA* donor–acceptor array. An infinite two-dimensional hydrogen-bonded network is formed instead.

Comment

The title compound, (I), was synthesized as part of a study on multiply hydrogen-bonded systems, focusing on the *DADA* motif in quadruply hydrogen-bonded dimers of triazines and pyrimidines (Beijer *et al.*, 1998). A review of quadruply hydrogen-bonded systems with several types of donor–acceptor arrays has recently been published by Sijbesma & Meijer (2003). When both ureido moieties adopt a particular *cis,trans* conformation, the title compound can arrange its hydrogen-bond donors and acceptors in such a way that a linear array of type *ADADA* (see Scheme) is formed. In this conformation, a quadruply hydrogen-bonded dimer can be formed. One of the peripheral acceptors is not directly involved in the formation of this dimer.



(I)

An atomic displacement ellipsoid plot of the title compound is given in Fig. 1, together with the atomic labelling scheme. Torsion angles describing the conformation of the ureido moieties are given in Table 1. One of the butylureido substituents of the triazine ring displays conformational disorder in the butyl moiety, as shown in Fig. 1. The disorder can be satisfactorily described with a two-site disorder model. The occupancy of the major component refined to a value of 0.533 (8).

Both ureido moieties adopt a *cis,trans* conformation, stabilized by intramolecular hydrogen bonds. The formation of a quadruply hydrogen-bonded dimer is, however, not observed in the crystalline state, because one of the intramolecular hydrogen bonds that stabilize the conformation of the molecule is donated to N103 (the triazine N located between the two ureido substituents) rather than towards N105 (a triazine N located between a ureido moiety and the methyl substituent). As a result, no linear array of type

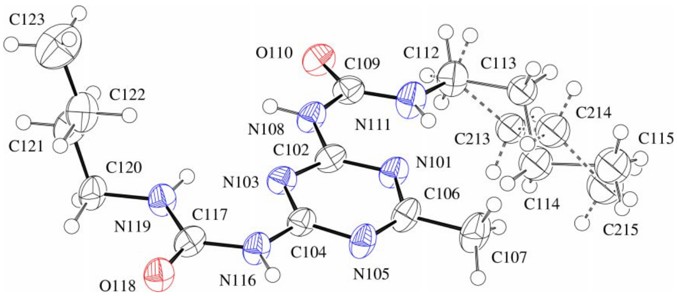


Figure 1
View of the title compound, with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary size. The minor disorder component is indicated by dashed bonds.

ADADA is formed, and dimerization *via* quadruple hydrogen-bonding is impossible. Instead, an infinite hydrogen-bonded network is present (see Fig. 2). The hydrogen bond donated by amine N108 links molecules related by a crystallographic twofold screw axis into chains running in the direction [010]. The graph set (Bernstein *et al.*, 1995) of this unitary motif is $C(4)$. These hydrogen-bonded chains of molecules are linked into a two-dimensional network through hydrogen bonds donated by amine N116. At the unitary level, this hydrogen bond forms dimers about a crystallographic inversion centre. The graph set of the hydrogen-bonded dimer is $R_2^2(8)$. Base vectors of the two-dimensional network are [010] and [001]. Geometric details of the hydrogen bonds are given in Table 2.

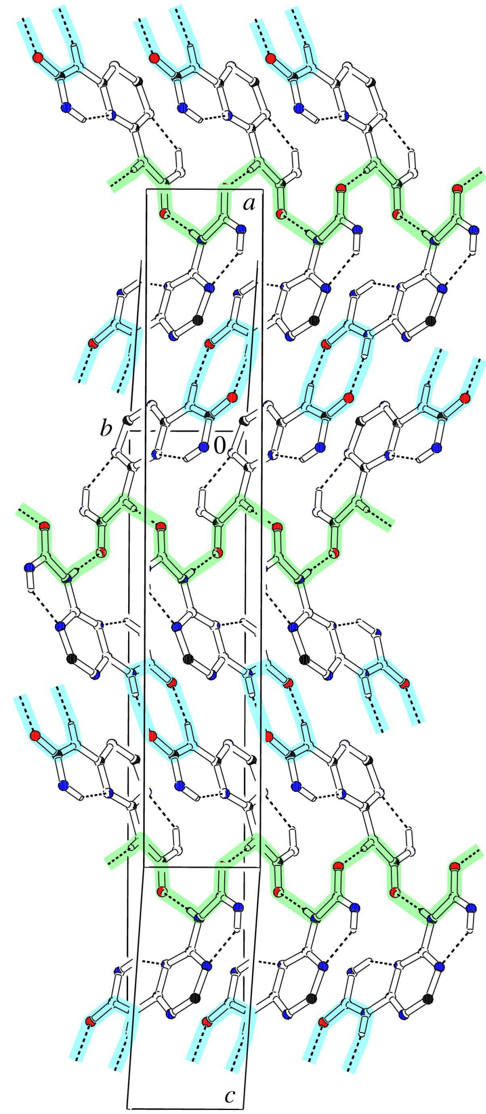


Figure 2
Two-dimensional hydrogen-bonded network. The butyl and methyl moieties, as well as the H atoms not involved in hydrogen bonding, have been omitted for clarity. The hydrogen-bond motifs with graph set $C(4)$ are highlighted in green, the motifs with graph set $R_2^2(8)$ are highlighted in blue.

Experimental

A suspension of 2,4-diamino-6-methyl-*s*-triazine (1.25 g, 10 mmol) and butyl isocyanate (11.3 ml, 100 mmol) in dry pyridine (50 ml) was heated under reflex for 16 h. After this period, water was added to the resultant solution to hydrolyse the excess of butyl isocyanate. After removal of the solvent, the resulting solid was crystallized from ethanol/water 2:1 *v*/*v*. Column chromatography (6% THF in chloroform), followed by crystallization from ethyl acetate and treatment with active carbon, gave an analytically pure sample (0.53 g, 16%), m.p. 502 K. ^{1}H-NMR ($CDCl_3$) δ: 10.17 (*br*), 9.05 (*br*), 3.32 (*q*, 4H), 2.42 (*s*, 3H), 1.52 (*m*, 4H), 1.34 (*m*, 4H), 0.89 (*t*, 6H). ^{13}C-NMR ($CDCl_3$) δ: 175.1, 162.8, 153.6, 39.4, 31.1, 25.2, 19.8, 13.3. IR (KBr) ν: 3407, 3266, 3203, 2956, 2930, 2918, 2871, 1704, 1684, 1593, 1526, 1479 cm^{-1}. Analysis: calcd. for $C_{14}H_{25}N_7O_2$: C, 52.0; H, 7.79; N: 30.32; found: C, 51.93; H, 7.70; N, 30.47.

Crystals suitable for X-ray structure determination were obtained by slow evaporation of a solution in ethanol.

Crystal data

$C_{14}H_{25}N_7O_2$
M_r = 323.41
Monoclinic, $C2/c$
a = 29.54 (2) Å
b = 4.613 (5) Å
c = 26.89 (2) Å
β = 109.34 (7)°
V = 3458 (5) Å^3
Z = 8
D_x = 1.242 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 8.2–17.1°
μ = 0.09 mm^{-1}
T = 150 K
Plate, colourless
0.50 × 0.10 × 0.04 mm

Data collection

Enraf–Nonius CAD-4 Turbo diffractometer
ω scans
Absorption correction: none
10715 measured reflections
3141 independent reflections
1113 reflections with $I > 2\sigma(I)$
R_{int} = 0.284
θ_{max} = 25.3°
$h = -34 \rightarrow 34$
$k = 0 \rightarrow 5$
$l = -32 \rightarrow 32$
3 standard reflections
frequency: 60 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.187
S = 1.11
3141 reflections
205 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected geometric parameters (°).

C109—N108—C102—N103	−174.1 (5)	C117—N116—C104—N103	0.6 (8)
C102—N108—C109—O110	172.3 (5)	C104—N116—C117—O118	175.4 (5)
C112—N111—C109—O110	−2.5 (9)	C120—N119—C117—O118	−2.9 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N108—H104···O110^{i}	0.88	1.99	2.861 (6)	173
N111—H105···N101	0.88	1.96	2.653 (6)	135
N116—H115···O118^{ii}	0.88	1.95	2.818 (5)	170
N119—H116···N103	0.88	2.01	2.690 (7)	133

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

H atoms were placed at calculated positions, riding on their carrier atoms. The H atoms of the methyl moieties were refined as rigid groups, allowing for rotation around the C—C bond. Isotropic displacement parameters of H atoms were set to 1.5 or 1.2 times the equivalent isotropic displacement parameter of the carrier atom for methyl and other H atoms, respectively. The C atoms of the major disorder component were refined with isotropic displacement parameters. The displacement parameters of the minor component atoms were equated to those of the corresponding atoms in the major component. The crystals of the title compound diffracted very poorly, displaying broad, weak reflections. The measured intensities therefore have a high standard uncertainty, as is shown by the value of R_σ [$= \Sigma\, \sigma(I)/\Sigma\, I$], which amounts to 0.1998. As a consequence, R~int~ is also relatively high. However, upon merging 13314 measured reflections into 3141 unique reflections, only 182 were found to be significantly inconsistent. Several batches of the compound were crystallized. A total of 6 different crystals were placed on the diffractometer. All of these showed poor diffraction. Full data were collected for three different crystals, all of which showed high R~int~ values (up to 0.42). After solving the structure, all data sets revealed essentially the same structure. None of the data sets showed any of the classic signs of twinning.H atoms were placed at calculated positions, riding on their carrier atoms.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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References

Beijer, F. H., Kooijman, H., Spek, A. L., Sijbesma, R. P., & Meijer E. W. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 75–78.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
Sheldrick, G. M. (1986). *SHELXS*86. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Sijbesma, R. P. & Meijer, E. W. (2003). *Chem. Commun.* pp 5–16.
Spek, A. L. (1997). *HELENA*. Utrecht University, The Netherlands.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.