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4-Amino-3,5-diethyl-4*H*-1,2,4-triazole at 100 K: chains of edge-fused $R_4^4(10)$ and $R_4^4(20)$ rings

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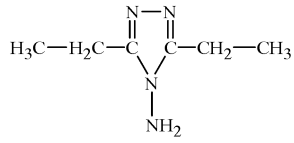
The title compound, $C_6H_{12}N_4$, has four crystallographically independent molecules in the asymmetric unit. Intermolecular N—H···N hydrogen bonds involving amino groups and triazole N atoms form a three-dimensional framework involving $R_4^4(10)$ and $R_4^4(20)$ rings. The hydrogen bonding is supported by weak C—H···π interactions.

Comment

1,2,4-Triazole and its derivatives have been used as starting materials for the synthesis of many heterocycles (Desenko, 1995). The triazole ring, having strong σ-donor and weak π-acceptor properties, potentially has two different coordination modes through three N donor atoms coordinating to metal ions (Van Diemen *et al.*, 1991; Ding *et al.*, 2004; Yi *et al.*, 2004; Ren *et al.*, 2006). Recent interest in substituted 1,2,4-triazoles has arisen in part from their transition metal complexes with intriguing structures and specific magnetic properties (Zhou *et al.*, 2005, 2006). Many metal complexes containing substituted 1,2,4-triazole have potential applications in molecular-based memory devices, displays and optical switches owing to their spin crossover properties (Garcia *et al.*, 1997; Kahn & Martinez, 1998). Apart from their chemical significance, 1,2,4-triazole derivatives have been found to be associated with diverse pharmacological properties, such as anti-inflammatory, antifungal and antiviral activities (Massa *et al.*, 1992; Mahomed *et al.*, 1993; Mullican *et al.*, 1993). Some are also known to exhibit analgesic, anticonvulsant, tranquilizing, antidepressant, anxiolytic (Bradbury & Rivett, 1991; Sughen & Yoloye, 1978; Stillings *et al.*, 1986; Kane *et al.*, 1988) or even antitumour activities (Hatheway *et al.*, 1978) and are applied in therapy (*e.g.* alprazolam, estazolam, triazolam and adinazolam; Budavari *et al.*, 1996). In spite of the chemical and medicinal importance of this class of compounds, relatively few crystal structures of 1,2,4-triazole derivatives have been reported (Cambridge Structural Database, Version 5.27 of November, 2005; Allen, 2002). In order to clarify the structure of this type of compound, an X-ray structure determination of the title compound, (I), has been carried out, and the results are presented here. The structure has been confirmed by IR, ^{1}H NMR and ^{13}C NMR spectroscopies and also by elemental analysis.



(I)

The molecular structure and atom-numbering scheme for (I) are shown in Fig. 1; selected bond lengths are given in Table 1. Compound (I) crystallizes in the space group *C*2/*c* with $Z' = 4$, and the hydrogen bonding was analysed with the aid of *PLATON* (Spek, 2003). The asymmetric unit contains four independent molecules with statistically equivalent metrical parameters but different conformations. The N1—N4, N5—N8, N9—N12 and N13—N16 bond lengths (Table 1) indicate single-bond character, whereas the N2—N3, N6—N7, N10—N11 and N14—N15 bond lengths are indicative of significant double-bond character. Similar N—N and N=N bond-length values have been observed in 4-amino-3-methyl-5-(*p*-tolyl)-4*H*-1,2,4-triazole and 4-amino-3-methyl-5-phenyl-4*H*-1,2,4-triazole [N—N = 1.4090 (16) and 1.4081 (18) Å, and N=N = 1.3859 (19) and 1.396 (2) Å; Şahin *et al.*, 2006]. The H atoms of the amino group form hydrogen bonds with the N atoms of neighbouring triazole rings. The geometric parameters of the N—H···N hydrogen-bonding interactions are given in Table 2.

Amino atom N4 in the reference molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H4*B*, to atom N7 within the asymmetric unit and, *via* H4*A*, to atom N6^{v} (symmetry codes are defined in the footnote of Table 2), so forming a centrosymmetric $R_4^4(10)(A)$ (Bernstein *et al.*, 1995) ring centred at ($\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{2}$). Similarly, amino atom N12 acts as a hydrogen-bond

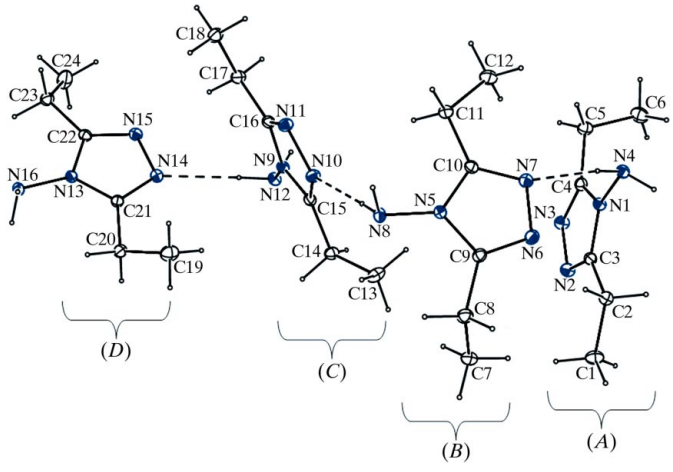


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

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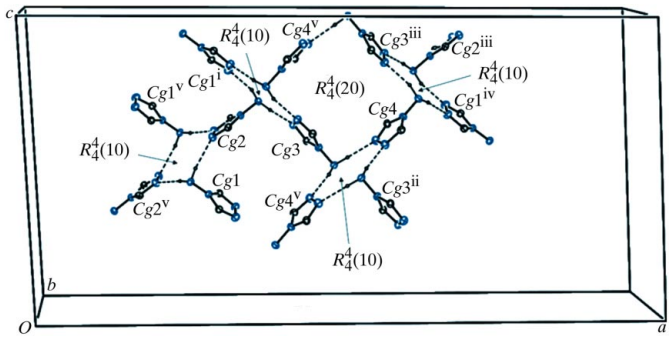

Figure 2
The packing of (I), showing the $R_4^4(10)$ and $R_4^4(20)$ ring patterns. Dashed lines indicate hydrogen bonds. H atoms not involved in these interactions and ethyl groups have been omitted for clarity. (Symmetry codes are provided in Table 2.)

donor, *via* H12*D*, to atom N14 within the asymmetric unit and, *via* H12*E*, to atom N15^{ii}, so forming a second centrosymmetric ring motif, this time of $R_4^4(10)(B)$ type, centred at $(\frac{1}{2}, 0, \frac{1}{2})$. The arrangement of the N8—H8*C*···N10, N8—H8*D*···N3^{i}, N16^{iii}—H16*A*^{iii}···N11 and N16^{iii}—H16*B*^{iii}···N2^{i} interactions can be described by the graph-set notation $R_4^4(10)(C)$. At the same time, the N16—H16*A*···N11^{iii}, N16—H16*B*···N2^{iv}, N8^{iii}—H8*C*^{iii}···N10^{iii} and N8^{iii}—H8*D*^{iii}···N3^{iv} interactions constitute an $R_4^4(10)(D)$ ring. Finally, the N12—H12*D*···N14, N16—H16*A*···N11^{iii}, N12^{iii}—H12*D*^{iii}···N14^{iii} and N16^{iii}—H16*A*^{iii}···N11 interactions produce an $R_4^4(20)(E)$ ring (Fig. 2).

Propagation of eight hydrogen bonds then forms a chain of edge-fused rings, containing $R_4^4(10)(A)R_4^4(10)(B)R_4^4(10)(C)$-$R_4^4(10)(D)$ sequences of four edge-fused rings. Similarly, edge-fused $R_4^4(10)(C)$ and $R_4^4(20)(E)$ rings form a chain running along the *c* axis. In compound (I), interlinked $C_4^4(20)$ anti-parallel chains zigzagging along the *a* axis are formed through N4^{v}—H4*A*^{v}···N6, N8—H8*C*···N10, N12—H12*D*···N14 and N16—H16*B*···N2^{iv} interactions. Amino atom N16 in the molecule at $(x, -y, -\frac{1}{2} + z)$ acts as hydrogen-bond donor, *via* H16*A*, to N11^{ii}, while N12^{ii} acts as donor to N15, and in this manner a $C_2^2(10)$ chain running parallel to the [001] direction is generated.

These intermolecular interactions, namely an extensive network of hydrogen bonds and π-ring interactions, are responsible for constructing an infinite three-dimensional framework.

Experimental

Propionic acid (18.5 g, 0.25 mol) was added to a solution of hydrazine hydrate (21.5 g, 0.4 mol) and the mixture was refluxed for 5 h. On cooling, a precipitate was formed, and this product was filtered off and dried. Recrystallization from ethyl acetate gave a colourless product (yield 62%). Single crystals of (I) were obtained from ethyl acetate at room temperature by slow evaporation (m.p. 438–439 K). IR (KBr, cm^{-1}): 3235–3120 (ν_{NH_2}), 1664 ($\nu_{C=N}$); ^{1}H NMR ($CDCl_3$): δ 1.30 (*t*, 6H, $2CH_3$), 2.76 (*g*, 4H, $2CH_2$), 5.02 (*s*, 2H, NH_2); ^{13}C NMR ($CDCl_3$): δ 156.21 (triazole C_3 and triazole C_5), 17.87 (CH_2), 11.40 (CH_3). Elemental analysis calculated for $C_6H_{12}N_4$: C 51.41, H 8.63, N 39.97%; found: C 52.40, H 8.61, N 39.75%.

Crystal data

$C_6H_{12}N_4$
M_r = 140.20
Monoclinic, *C*2/*c*
a = 37.782 (2) Å
b = 9.2996 (4) Å
c = 18.4055 (12) Å
β = 93.067 (5)°
V = 6457.6 (7) Å^3
Z = 32
Mo *K*α radiation
μ = 0.08 mm^{-1}
T = 100 K
0.50 × 0.48 × 0.41 mm

Data collection

Stoe IPDSII diffractometer
16583 measured reflections
6331 independent reflections
4902 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.091
S = 1.04
6331 reflections
393 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected bond lengths (Å).

N1—N4	1.4130 (14)	N9—N12	1.4109 (14)
N2—N3	1.3997 (15)	N10—N11	1.4016 (14)
N5—N8	1.4118 (14)	N13—N16	1.4119 (14)
N6—N7	1.3981 (15)	N14—N15	1.3984 (15)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N8—H8*C*···N10	0.910 (17)	2.192 (17)	3.0975 (15)	173.4 (14)
N8—H8*D*···N3^{i}	0.923 (19)	2.088 (19)	2.9645 (16)	158.2 (15)
N12—H12*D*···N14	0.929 (16)	2.108 (16)	3.0295 (15)	171.6 (14)
N12—H12*E*···N15^{ii}	0.952 (16)	2.127 (17)	3.0650 (16)	168.0 (13)
N16—H16*A*···N11^{iii}	0.931 (17)	2.112 (18)	3.0256 (16)	166.7 (14)
N16—H16*B*···N2^{iv}	0.942 (17)	2.070 (17)	3.0066 (15)	172.9 (14)
N4—H4*A*···N6^{v}	0.888 (16)	2.195 (17)	3.0803 (15)	174.8 (14)
N4—H4*B*···N7	0.925 (18)	2.161 (18)	3.0736 (16)	168.8 (14)

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

All H atoms bound to carbon were refined using a riding model, with C—H distances of 0.97 Å [U_{iso}(H) = 1.2U_{eq}(parent atom)] for methylene H atoms and 0.96 Å [U_{iso}(H) = 1.5U_{eq}(parent atom)] for methyl H atoms. The amino H atoms were located in a difference map and were refined freely (distances are given in Table 2).

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3081). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bradbury, R. H. & Rivett, J. E. (1991). *J. Med. Chem.* **34**, 151–157.

Budavari, S., O'Neil, M. J., Smith, A., Heckelman, P. E. & Kinnearty, J. F. (1996). Editors. *The Merck Index*, 12th ed., entries 159, 320, 3744 and 9734. New Jersey: Merck and Co. Inc.

Desenko, S. M. (1995). *Khim. Geterotsikl. Soedin.* (*Chem. Heterocycl. Comput.*), pp. 2–24.

Ding, B., Yi, L., Zhu, L.-N., Cheng, P. & Liao, D.-Z. (2004). *J. Coord. Chem.* **57**, 9–16.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Garcia, Y., van Koningsbruggen, P. J., Codjovi, E., Lapouyade, R., Kahn, O. & Rabardel, L. (1997). *J. Mater. Chem.* **7**, 857–858.

Hatheway, G. J., Hansch, C., Kim, K. H., Milstein, S. R., Schmidt, C. L., Smith, R. N. & Quinn, F. R. (1978). *J. Med. Chem.* **21**, 563–567.

Kahn, O. & Martinez, C. J. (1998). *Science*, **279**, 44–48.

Kane, J. M., Dudley, M. W., Sorensen, S. M. & Miller, F. P. (1988). *J. Med. Chem.* **31**, 1253–1258.

Mahomed, E. A., El-Deen, I. M., Ismail, M. M. & Mahomed, S. M. (1993). *Indian J. Chem. Sect. B*, **32**, 933–937.

Massa, S., Di Santo, R., Retico, A., Artico, M., Simonetti, N., Fabrizi, G. & Lamba, D. (1992). *Eur. J. Med. Chem.* **27**, 495–502.

Mullican, M. D., Wilson, M. W., Connor, D. T., Kostlan, C. R., Schrier, D. J. & Dyer, R. D. (1993). *J. Med. Chem.* **36**, 1090–1099.

Ren, P., Ding, B., Shi, W., Wang, Y., Lu, T. & Cheng, P. (2006). *Inorg. Chim. Acta*, **359**, 3824–3830.

Şahin, O., Büyükgüngör, O., Şaşmaz, S., Gümrükçüoğlu, N. & Kantar, C. (2006). *Acta Cryst.* C**62**, o643–o646.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Stillings, M. R., Welbourn, A. & Walter, D. S. (1986). *J. Med. Chem.* **29**, 2280–2284.

Stoe & Cie (2002). *X-RED* and *X-AREA*. Stoe & Cie, Darmstadt, Germany.

Sughen, J. K. & Yoloye, T. (1978). *Pharm. Acta Helv.* **58**, 64–68.

Van Diemen, J. H., Haasnoot, J. G., Hage, R., Reedijk, J., Vos, J. G. & Wang, R. (1991). *Inorg. Chem.* **30**, 4038–4043.

Yi, L., Ding, B., Zhao, B., Cheng, P., Liao, D.-Z., Yan, S.-P. & Jiang, Z.-H. (2004). *Inorg. Chem.* **43**, 33–43.

Zhou, J.-H., Cheng, R.-M., Song, Y., Li, Y.-Z., Yu, Z., Chen, X.-T., Xue, Z.-L. & You, X.-Z. (2005). *Inorg. Chem.* **44**, 8011–8022.

Zhou, J.-H., Cheng, R.-M., Song, Y., Li, Y.-Z., Yu, Z., Chen, X.-T. & You, X.-Z. (2006). *Polyhedron*, **25**, 2426–2432.