Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

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

Onur Şahin,[a]* Orhan Büyükgüngör,[a] Selami Şaşmaz,[b] Nurhan Gümrükçüoğlu[c] and Cihan Kantar[b]

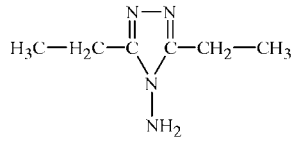
[a]Department of Physics, Ondokuz Mayıs University, TR-55139 Samsun, Turkey, [b]Department of Chemistry, Rize University, Turkey, and [c]Department of Chemistry, Giresun University, Turkey
Correspondence e-mail: onurs@omu.edu.tr

Received 11 March 2007
Accepted 29 May 2007
Online 23 June 2007

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

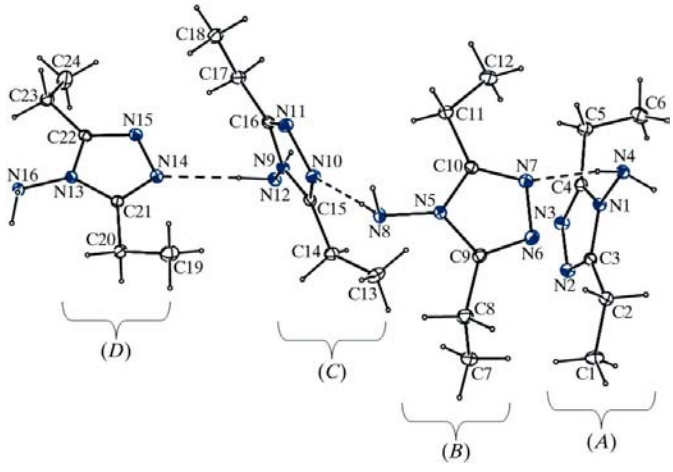


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

 DOI: 10.1107/S0108270107026339 © 2007 International Union of Crystallography

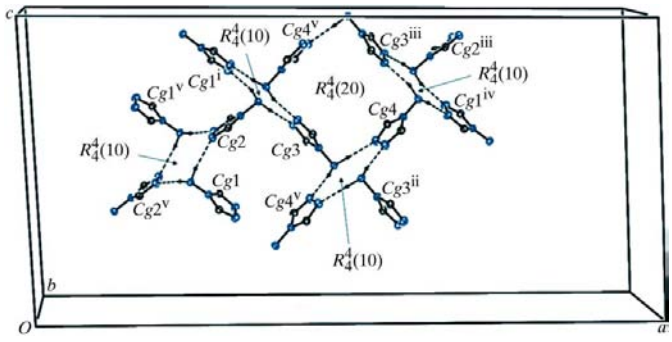


Figure 2
The packing of (I), showing the $R_4^4(10)$ and $R_4^4(20)$ ring patterns. Dashed lines indicate hydrogen bonds. H atoms not involved in these interactions and ethyl groups have been omitted for clarity. (Symmetry codes are provided in Table 2.)

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).

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDSII diffractometer (purchased under grant No. F279 of the University Research Fund).

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.