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A new polymorph of 5,5'-(ethane-1,2-diyl)bis(1*H*-tetrazole)Cheng-Fang Qiao,^a Chun-Sheng Zhou,^{a*} Qing Wei^b and Zheng-Qiang Xia^b^aDepartment of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Comprehensive Utilization of Tailing Resources, Shangluo University, Shangluo 726000, Shaanxi, People's Republic of China, and ^bCollege of Chemistry and Materials Science, Northwest University, Xi'an 710069, Shaanxi, People's Republic of China

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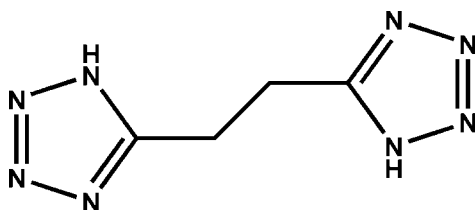
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.037; wR factor = 0.098; data-to-parameter ratio = 8.6.

The asymmetric unit of the title compound, $\text{C}_4\text{H}_6\text{N}_8$, contains a quarter of the molecule, which possesses a crystallographically imposed centre of symmetry with all non-H atoms situated on a mirror plane. The crystal packing exhibits intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds and $\pi-\pi$ stacking interactions between the tetrazole rings of adjacent molecules [centroid-centroid distance = 3.4402 (10) Å].

Related literature

For the previously reported polymorph, see: Shen *et al.* (2011). For the synthesis of the title compound and for related structures, see: Chafin *et al.* (2008); Diop *et al.* (2002). For the application of tetrazole derivatives in coordination chemistry and energetic materials, see: Zhao *et al.* (2008); Singh *et al.* (2006).



Experimental

Crystal data

 $\text{C}_4\text{H}_6\text{N}_8$ $M_r = 166.17$

Monoclinic, $C2/m$
 $a = 10.951$ (3) Å
 $b = 6.678$ (2) Å
 $c = 5.0329$ (14) Å
 $\beta = 114.250$ (4)°
 $V = 335.58$ (17) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 296$ K
 $0.31 \times 0.27 \times 0.13$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.962$, $T_{\max} = 0.985$

819 measured reflections
 320 independent reflections
 293 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.098$
 $S = 1.09$
 320 reflections

37 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{N4}-\text{H4}\cdots\text{N2}^i$ | 0.86 | 2.10 | 2.943 (3) | 166 |

Symmetry code: (i) $x, y, z + 1$.

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5246).

References

- Bruker (2008). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chafin, A., Irvin, D. J., Mason, M. H. & Mason, S. L. (2008). *Tetrahedron Lett.* **49**, 3823–3826.
 Diop, C. A. K., Mahon, M. F., Molloy, K. C., Ooi, L., Raithby, P. R., Venter, M. M. & Teat, S. J. (2002). *CrystEngComm*, **4**, 462–466.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Shen, L., Yang, J., Yang, G. W., Li, Q. Y., Tang, X. Y., Zhou, F., Miao, Z. F., Jin, J. N. & Shen, W. (2011). *Inorg. Chim. Acta*, **370**, 150–155.
 Singh, R. P., Verma, R. D., Meshri, D. T. & Shreeve, J. M. (2006). *Angew. Chem. Int. Ed.* **45**, 3584–3601.
 Zhao, H., Qu, Z. R., Ye, H. Y. & Xiong, R. G. (2008). *Chem. Soc. Rev.* **37**, 84–100.

supplementary materials

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A new polymorph of 5,5'-(ethane-1,2-diyl)bis(1*H*-tetrazole)

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Comment

Due to the rich coordination modes and high content of nitrogen, tetrazole compounds have been studied for more than one hundred years and widely applied in coordination chemistry (Zhao *et al.*, 2008) and energetic materials (Singh *et al.*, 2006). As an important derivative of tetrazole, 5,5'-ethane-1,2-diylbis(1*H*-tetrazole) has been utilized to construct functional and interesting coordination compounds owing to its flexible coordination modes. The crystal structure of the title compound has been previously reported by Shen *et al.* (2011) in the monoclinic space group $P2_1/c$ ($Z = 4$). We report here the synthesis and crystal structure of a new polymorph of the title compound, (**I**).

Polymorph **I** crystallizes in the space group $C2/m$ ($Z = 2$) with one-fourth part of the molecule in the asymmetric unit. In the crystal, all non-H atoms are situated on the mirror plane. Similar to the previously reported polymorph, each pair tetrazolate rings in **I** are coplanar linked by flexible $-\text{CH}_2-\text{CH}_2-$ group (Fig. 1). The bond lengths and angles in **I** are within normal ranges and comparable with the previously reported structure. $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds (Table 1) link the adjacent molecules into one-dimensional belts along the c axis, whereas molecules of the previously reported polymorph are connected into a three dimensional supramolecular framework. The $\text{N}\cdots\text{N}$ distance [2.943 (3) Å] is longer than that seen in the previously published polymorph [2.840 (2) and 2.873 (2) Å] (Shen *et al.*, 2011). π - π stacking interactions between tetrazole rings of adjacent molecules [centroid-centroid distances = 3.4402 (10) Å] further consolidate the crystal packing.

Experimental

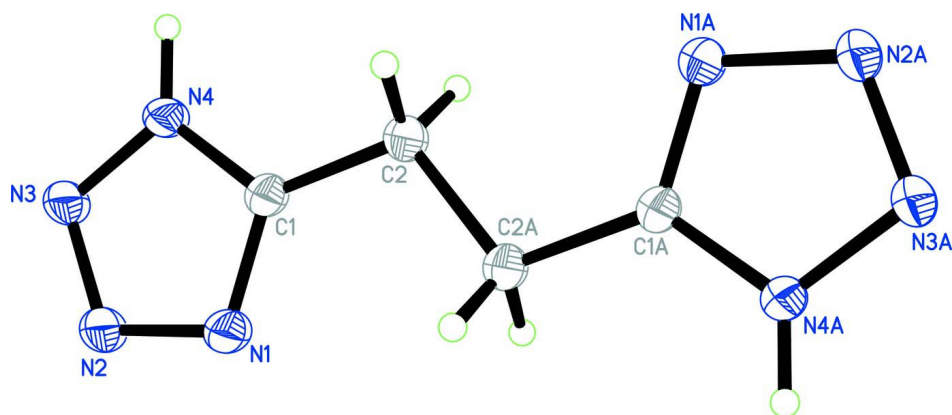
The title compound was prepared from a mixture of sodium azide and succinonitrile using the method described by Chafin *et al.* (2008). Colourless block single crystals were obtained by recrystallization of the title compound from ethanol.

Refinement

All H atoms were positioned geometrically ($\text{C}-\text{H} = 0.97$ Å and $\text{N}-\text{H} = 0.86$ Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C},\text{N})$.

Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

**Figure 1**

The molecular structure of **I** showing the atomic numbering and 30% probability displacement ellipsoids [symmetry code: (A) $-x, y, -z$].

5,5'-(Ethane-1,2-diyl)bis(1H-tetrazole)

Crystal data

$C_4H_6N_8$

$M_r = 166.17$

Monoclinic, $C2/m$

Hall symbol: $-C 2y$

$a = 10.951 (3) \text{ \AA}$

$b = 6.678 (2) \text{ \AA}$

$c = 5.0329 (14) \text{ \AA}$

$\beta = 114.250 (4)^\circ$

$V = 335.58 (17) \text{ \AA}^3$

$Z = 2$

$F(000) = 172$

$D_x = 1.644 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 501 reflections

$\theta = 3.7\text{--}25.9^\circ$

$\mu = 0.12 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, colorless

$0.31 \times 0.27 \times 0.13 \text{ mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2008)

$T_{\min} = 0.962$, $T_{\max} = 0.985$

819 measured reflections

320 independent reflections

293 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 24.9^\circ$, $\theta_{\min} = 3.7^\circ$

$h = -7 \rightarrow 12$

$k = -7 \rightarrow 7$

$l = -5 \rightarrow 5$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.098$

$S = 1.09$

320 reflections

37 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 0.15P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.17 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|--------------|----------|-------------|----------------------------------|-----------|
| N1 | 0.19695 (18) | 0.0000 | -0.1482 (4) | 0.0402 (6) | |
| N2 | 0.3293 (2) | 0.0000 | -0.0872 (4) | 0.0407 (6) | |
| N3 | 0.4005 (2) | 0.0000 | 0.1919 (4) | 0.0393 (6) | |
| N4 | 0.31215 (19) | 0.0000 | 0.3136 (4) | 0.0355 (6) | |
| H4 | 0.3323 | 0.0000 | 0.4977 | 0.043* | |
| C1 | 0.1877 (2) | 0.0000 | 0.1035 (5) | 0.0327 (6) | |
| C2 | 0.0608 (2) | 0.0000 | 0.1451 (5) | 0.0378 (6) | |
| H2A | 0.0582 | 0.1175 | 0.2559 | 0.045* | 0.50 |
| H2B | 0.0582 | -0.1175 | 0.2559 | 0.045* | 0.50 |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|----------|-------------|----------|
| N1 | 0.0237 (11) | 0.0681 (14) | 0.0269 (12) | 0.000 | 0.0087 (9) | 0.000 |
| N2 | 0.0244 (11) | 0.0676 (14) | 0.0314 (12) | 0.000 | 0.0129 (9) | 0.000 |
| N3 | 0.0238 (10) | 0.0650 (13) | 0.0305 (11) | 0.000 | 0.0127 (8) | 0.000 |
| N4 | 0.0230 (10) | 0.0589 (12) | 0.0233 (10) | 0.000 | 0.0082 (8) | 0.000 |
| C1 | 0.0227 (12) | 0.0475 (13) | 0.0256 (11) | 0.000 | 0.0076 (9) | 0.000 |
| C2 | 0.0200 (13) | 0.0643 (15) | 0.0278 (13) | 0.000 | 0.0085 (10) | 0.000 |

Geometric parameters (\AA , $^\circ$)

| | | | |
|----------|-------------|-------------------------|-----------|
| N1—C1 | 1.312 (3) | N4—H4 | 0.8600 |
| N1—N2 | 1.353 (3) | C1—C2 | 1.488 (3) |
| N2—N3 | 1.297 (3) | C2—C2 ⁱ | 1.519 (4) |
| N3—N4 | 1.341 (3) | C2—H2A | 0.9700 |
| N4—C1 | 1.338 (3) | C2—H2B | 0.9700 |
| C1—N1—N2 | 106.33 (19) | N4—C1—C2 | 126.6 (2) |
| N3—N2—N1 | 110.93 (18) | C1—C2—C2 ⁱ | 111.4 (2) |
| N2—N3—N4 | 105.61 (18) | C1—C2—H2A | 109.3 |
| C1—N4—N3 | 109.32 (18) | C2 ⁱ —C2—H2A | 109.3 |
| C1—N4—H4 | 125.3 | C1—C2—H2B | 109.3 |
| N3—N4—H4 | 125.3 | C2 ⁱ —C2—H2B | 109.3 |
| N1—C1—N4 | 107.8 (2) | H2A—C2—H2B | 108.0 |
| N1—C1—C2 | 125.6 (2) | | |

| | | | |
|-------------|-------|--------------------------|-------|
| C1—N1—N2—N3 | 0.0 | N3—N4—C1—N1 | 0.0 |
| N1—N2—N3—N4 | 0.0 | N3—N4—C1—C2 | 180.0 |
| N2—N3—N4—C1 | 0.0 | N1—C1—C2—C2 ⁱ | 0.0 |
| N2—N1—C1—N4 | 0.0 | N4—C1—C2—C2 ⁱ | 180.0 |
| N2—N1—C1—C2 | 180.0 | | |

Symmetry code: (i) $-x, -y, -z$.

Hydrogen-bond geometry (Å, °)

| <i>D—H</i> ⋯ <i>A</i> | <i>D—H</i> | <i>H</i> ⋯ <i>A</i> | <i>D</i> ⋯ <i>A</i> | <i>D—H</i> ⋯ <i>A</i> |
|------------------------|------------|---------------------|---------------------|-----------------------|
| N4—H4⋯N2 ⁱⁱ | 0.86 | 2.10 | 2.943 (3) | 166 |

Symmetry code: (ii) $x, y, z+1$.