Crystal Structure of 1-methoxy-2,2,2-tris(pyrazol-1-yl)ethane

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Lyubartseva, Ganna; Parkin, Sean; Coleman, Morgan D.; and Mallik, Uma Prasad, "Crystal Structure of 1-methoxy-2,2,2-tris(pyrazol-1-yl)ethane" (2014). Chemistry Faculty Publications. Paper 31.
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Crystal structure of 1-methoxy-2,2,2-tris(pyrazol-1-yl)ethane

Ganna Lyubartsevaa,* Sean Parkin,b Morgan D. Colemana and Uma Prasad Mallikc

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Received 17 August 2014; accepted 18 August 2014

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

The title compound, C12H14N6O, consists of three pyrazole rings bound via nitrogen to the distal ethane carbon of methoxy ethane. The dihedral angles between the three pyrazole rings are 67.62 (14), 73.74 (14), and 78.92 (12). In the crystal, molecules are linked by bifurcated C—H···N hydrogen bonds, forming double-stranded chains along [001]. The chains are linked via C—H···O hydrogen bonds, forming a three-dimensional framework structure. The crystal was refined as a perfect (0.5:0.5) inversion twin.

Keywords: crystal structure; tris(pyrazol-1-yl)ethane; scorpionate ligands.

CCDC reference: 1019968

1. Related literature

For properties of pyrazole-based tridentate ligands, see: Paulo et al. (2004); Bigmore et al. (2005). For nickel and cobalt complexes of N-donor tridentate scorpionate ligands, see: Lyubartseva et al. (2011, 2012, 2013a,b); Lyubartseva & Parkin (2009). For the synthesis of the title compound, see: Maria et al. (2007).

2. Experimental

2.1. Crystal data

C12H14N6O

M_r = 258.29

Monoclinic, Cc

a = 12.5828 (3) Å

b = 12.3847 (3) Å

c = 8.4007 (2) Å

β = 102.5635 (11)°

V = 1289.94 (5) Å³

Z = 4

Mo Kα radiation

μ = 0.09 mm⁻¹

T = 90 K

0.28 × 0.20 × 0.16 mm

2.2. Data collection

Nonius KappaCCD diffractometer

Absorption correction: multi-scan

T( min) = 0.749, T(max) = 0.942

2934 independent reflections

2386 reflections with I > 2σ(I)

Rint = 0.032

2.3. Refinement

R[F² ≥ 2σ(F²)] = 0.042

wR(F²) = 0.102

S = 1.10

Hydrogen-bond geometry (Å, °).

Table 1

\[ \begin{array}{cccc}
\text{D--H···A} & \text{D--H} & \text{H···A} & \text{D···A} \\
\hline
C5--H5A···N2i  & 0.95 & 2.51 & 3.453 (4) & 171 \\
C9--H9A···N2ii & 0.95 & 2.61 & 3.433 (4) & 145 \\
C4--H4A···O1iii & 0.95 & 2.53 & 3.444 (4) & 162 \\
\end{array} \]

Symmetry codes: (i) x, −y + 1, z + 1/2; (ii) x, y, z + 1; (iii) x + 1, −y + 1/2, z + 1.

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO-SMN (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1996); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2008); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL2014 and PLATON (Spek, 2009).

Acknowledgements

GL is grateful to the Southern Arkansas University Faculty Research Grant for financial support.

Supporting information for this paper is available from the IUCr electronic archives (Reference: SU2774).

References


Maria et al. (2007).


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S1. Synthesis and crystallization
The title compound was prepared using the published procedure (Maria et al., 2007). Colourless block-like crystals were obtained by slow evaporation of a diethyl ether solution of pure product. Spectral and other characterizations are in good accordance with the previously reported data (Maria et al., 2007).

S2. Refinement
H atoms were located in difference Fourier maps, but were subsequently included in the refinement using a riding model approximation: C—H = 0.95 - 0.99 Å with Uiso(H) = 1.5Ueq(C-methyl) and = 1.2Ueq(C) for other H atoms. The crystal was refined as a perfect (0.5:0.5) inversion twin.

Figure 1
View of molecular structure of the title molecule, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.
1-Methoxy-2,2,2-tris(pyrazol-1-yl)ethane

Crystal data

C₁₂H₁₄N₆O  
F(000) = 544  
Dₐ = 1.330 Mg m⁻³  
Mo Kα radiation, λ = 0.71073 Å  
Cell parameters from 1549 reflections  
θ = 1.0–27.5°  
µ = 0.09 mm⁻¹  
T = 90 K  
Block, colourless  
0.28 × 0.20 × 0.16 mm

F(000) = 544  
Dₐ = 1.330 Mg m⁻³  
Mo Kα radiation, λ = 0.71073 Å  
Cell parameters from 1549 reflections  
θ = 1.0–27.5°  
µ = 0.09 mm⁻¹  
T = 90 K  
Block, colourless  
0.28 × 0.20 × 0.16 mm

Data collection

Nonius KappaCCD  
diffractometer  
Radiation source: fine-focus sealed-tube  
Detector resolution: 9.1 pixels mm⁻¹  
φ and ω scans at fixed χ = 55°  
Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)  
Tmin = 0.749, Tmax = 0.942  
11397 measured reflections  
2934 independent reflections  
2386 reflections with I > 2σ(I)  
Rint = 0.032  
θmax = 27.5°, θmin = 2.3°  
h = −16→16  
k = −16→16  
l = −10→11

Refinement

Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.042  
wR(F²) = 0.102  
S = 1.10  
2934 reflections  
174 parameters  
2 restraints  
Hydrogen site location: difference Fourier map  
H-atom parameters constrained  
where P = (F² + 2Fc²)/3  
(Δ/σ)max < 0.001  
Δρmax = 0.23 e Å⁻³  
Δρmin = −0.18 e Å⁻³  
Extinction correction: SHELXL2014 (Sheldrick, 2008), Fe = kFc[1+0.0001xFc²/λ²sin(2θ)]¹/4  
Extinction coefficient: 0.0127 (19)  
Absolute structure: Refined as a perfect (i.e. 50:50) inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

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Experimental. The crystal was mounted with polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid nitrogen based cryostat, according to published methods (Hope, 1994; Parkin & Hope, 1998).

Diffraction data were collected with the crystal at 90 K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

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 progress was checked using PLATON (Spek, 2009) and by an R-tensor (Parkin, 2000). The final model was further checked with the IUCr utility checkCIF.
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**Supporting Information**

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C4—C3—C2 104.4 (3) H11A—C11—H11B 108.1
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C2—C3—H3A 127.8 O1—C12—H12B 109.5
N1—C4—C3 107.1 (3) H12A—C12—H12B 109.5
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N4—C5—C6 112.0 (3) H12B—C12—H12C 109.5
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C4—N1—C1—C11 −158.9 (3) N5—N6—C8—C9 −0.2 (4)
C10—N5—C1—C11 −115.6 (3) N6—N5—C10—C9 −0.6 (3)
N6—N5—C1—N3 −179.9 (2) C1—N5—C10—C9 −177.7 (3)
C10—N5—C1—N3 −61.3 (3) C8—C9—C10—N5 0.4 (3)
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N6—N5—C1—N3 −125.4 (3) C8—C9—C10—N5 0.4 (3)
C4—N1—C1—N3 78.6 (3) C5—C6—C7—N3 −0.2 (4)
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Hydrogen-bond geometry (Å, °)

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Symmetry codes: (i) x, −y+1, z+1/2; (ii) x, y, z+1; (iii) x+1/2, −y+1/2, z+1/2.