Trimethylpyrazole: a simple heterocycle reflecting Kitaigorodskii’s packing principle

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The five-membered heterocycle 1,3,5-trimethyl-1H-pyrazole, C₆H₁₀N₂ (I) crystallizes in space group Pnma with all non-hydrogen atoms of the molecule on the crystallographic mirror plane. This arrangement has been recognized as favorable with respect to space filling by Kitaigorodskii and Wilson, pioneers in the field of crystal packing; Pnma represents a particularly rare space group for residues exclusively in a general position. Neighboring molecules in I interact via non-classical C—H⋯N bonds in the plane and C—H⋯π contacts between adjacent layers. In Pnma, crystallographic inversion relates dipolar molecules located on successive mirror planes and results in their head-to-tail arrangement. The interlayer distance in the [010] direction is closely related to the van der Waals radii of C and N.

1. Introduction

Aleksander Kitaigorodskii was already working on his principle of close packing in the 1940s, at a time when structure analysis via single-crystal diffraction was still not fast and routine. We recall that about 20 years later, in 1965, the archives of the Cambridge Crystallographic Data Centre comprised only 3000 structures. Kitaigorodskii’s finding that void space in crystals is in general unfavorable enabled him to rank certain space groups as more or less suitable for close packing. It took considerable time before Kitaigorodskii’s ideas were appreciated in the western world (Kitaigorodskii, 1961, 1965, 1973). The term symmorphic refers to space groups that exhibit a special position with the same symmetry as the crystal class (Chapuis et al., 2022). A. J. C. Wilson expanded these original ideas (Wilson, 1993a) and coined the term antimorphic space groups (Wilson, 1993b), which only possess symmetry elements associated with a favorable packing, i.e. screw axes, glide planes and inversion centers. In contrast to Kitaigorodskii, W. Nowacki explained the statistical preference for certain space groups by their ability to form a favorable dipole arrangement rather than an efficient packing (Nowacki, 1943, 1951). An excellent summary of the close-packing principle and its consequences for space-group frequencies, together with other packing criteria, was published by Brock & Dunitz (1994).

In this contribution, we present the crystal structure of the simple heterocycle 1,3,5-trimethyl-1H-pyrazole (I) in space...
2. Results and Discussion

All non-hydrogen atoms in 1 occupy a crystallographic mirror plane in space group Pnma (Wyckoff position 4c), resulting in a strictly planar scaffold. A displacement ellipsoid plot of a heterocyclic molecule is shown in Fig. 1.

Compared to other simple pyrazoles, this is a unique property as most of them do not crystallize in space groups exhibiting a mirror plane, e.g. 1H-pyrazole (space groups Pna21 and Pbnm; Sikora & Katrusiak, 2013), 3,5-dimethyl-1H-pyrazole (space group R3c; Baldy et al., 1985) or 1,5-dimethyl-1H-pyrazole-3-carboxylic acid ethyl ester (PT; Schmidt et al., 2003). Intramolecular distances and angles in these pyrazoles and 1 are very similar and adopt values within a narrow range (Table 1).

**Pnma**, the space-group type adopted by the title compound, plays a central role in the concepts of Kitaigorodskii and Wilson. We cite literally from Wilson (1991): ‘The space-group plays a central role in the concepts of Kitaigorodskii and Wilson’s ideas.

group Pnma and describe its crystal packing in the context of Kitaigorodskii’s and Wilson’s ideas.

<table>
<thead>
<tr>
<th>Compound</th>
<th>d(N1—N2) (Å)</th>
<th>d(N2—C1) (Å)</th>
<th>d(N1—C3) (Å)</th>
<th>d(C2—C3) (Å)</th>
<th>d(C1—C2) (Å)</th>
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<tr>
<td>1</td>
<td>1.358 (4)</td>
<td>1.351 (4)</td>
<td>1.336 (4)</td>
<td>1.392 (4)</td>
<td>1.360 (5)</td>
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<td>PYRZOL27</td>
<td>1.357 (2)</td>
<td>1.358 (3)</td>
<td>1.334 (3)</td>
<td>1.391 (3)</td>
<td>1.373 (3)</td>
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<td>ALOSE2</td>
<td>1.3464 (17)</td>
<td>1.3595 (14)</td>
<td>1.3415 (16)</td>
<td>1.3966 (15)</td>
<td>1.377 (2)</td>
</tr>
</tbody>
</table>

References: (a) Sikora & Katrusiak (2013); (b) Schmidt et al. (2003).

Table 2

Comparison of N· · · H—C contacts (Å, °) observed in 1 and selected other pyrazoles.

<table>
<thead>
<tr>
<th>Compound</th>
<th>d(N· · · H) (Å)</th>
<th>∠(N· · · H—C) (°)</th>
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<tr>
<td>1</td>
<td>2.56</td>
<td>179</td>
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<tr>
<td>ICEDUQ*</td>
<td>2.852 (19)</td>
<td>177.3 (12)</td>
</tr>
<tr>
<td>LUNYID*</td>
<td>2.66</td>
<td>154</td>
</tr>
<tr>
<td>KITNOR*</td>
<td>2.458 (16)</td>
<td>156.2 (13)</td>
</tr>
</tbody>
</table>

References: (a) Patra et al. (2004); (b) Benisvy et al. (2009); (c) Kidwai et al. (2008).

The heterocyclic molecule in 1 is a candidate par excellence for Pnma: It not only matches the required site symmetry but all of its non-hydrogen atoms are located on this mirror plane, providing an efficient in-plane arrangement (Fig. 2, left).

Non-classical C—H· · · N hydrogen bonds represent the shortest directional contacts in the mirror plane and lead to chains along [100] (Fig. 2, right). This kind of interaction is quite common for 4-unsubstituted pyrazoles and we only provide selected examples for comparison: ICEDUQ (Patra et al., 2004), LUNYID (Benisvy et al., 2009) and KITNOR (Kidwai et al., 2008) (Table 2).

A crystallographic center of inversion (Wyckoff position 4a) relates objects on the mirror planes at y = 0.25 and y = 0.75; the dipole moments of consecutive layers are therefore oriented in opposite directions, quite in agreement with early Nowacki (1943) ideas. The non-planar methyl groups in 1

![Displacement ellipsoid plot (Spek, 2020) of a molecule in 1; ellipsoids are drawn at 70% probability. H atoms are shown as spheres of arbitrary radii. Selected distances (Å) and angles (°): N1—N2 1.358 (4), N2—C1 1.351 (4), C1—C2 1.360 (5), C2—C3 1.392 (4), N2—C4 1.448 (4), C3—N1—N2 104.2 (3), C1—C2—C3 106.6 (3).](Image78x110 to 252x257)

**Figure 1**

![Packaging in the (010) plane (Spek, 2020). Non-classical C—H· · · N contacts are shown as dashed lines: d(N· · · H*) = 2.56 Å; ∠(C*—H*—N) = 179°. Symmetry code: (a) −x, 1/2 + y, −z.](Image315x104 to 564x238)

**Figure 2**
provide the most relevant interlayer contacts. Fig. 3 shows the
head-to-tail arrangement of two molecules, with a methyl H
atom pointing towards the center of gravity of the five-
membered ring of a neighbor. The shortest interatomic
distance associated with this contact amounts to $H_{4b}/C_1/C_1/C_1/N_2$
[symmetry code: ($a$)1/C0x, C0y,1/C0z] = 2.65 Å.

The Hirshfeld surface (Spackman & Jayatilaka, 2009) about
one pyrazole moiety is shown in Fig. 4. It has been mapped
with the dimensionless interaction-sensitive quantity $d_{norm}$;
red areas indicate short contacts. Both the C—H $/C_1/C_1/C_1/N$
hydrogen bond and the interlayer methyl $/C_1/C_1/C_1/C_25$
contact can clearly be perceived.

The stacking of efficiently packed layers of which only the
methyl H atoms protrude leads to a simple relationship
between the lattice parameter in the stacking direction, i.e.
unit-cell parameter $b$ in the standard setting of space group
$Pnma$, and the van der Waals radii of the partaking atoms.
Fig. 5 provides a sketch of the situation.

Kitaigorodskii himself had determined van der Waals radii
($r_{vdW}$) of 1.8 Å for carbon and of 1.58 Å for nitrogen (Kita-
gorodskii, 1973); values of 1.7 for C and 1.55 for N have been
suggested by Batsanov (1995). The unit-cell parameter $b$ for
our title compound 1 amounts to approximately 6.7 Å, closely

Table 3
Other structures showing the same motif as 1: $r_{vdW}(C) = 1.7$ Å; $r_{vdW}(N) = 1.55$ Å (Batsanov, 1995).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>$b$ (Å)</th>
<th>$b/4$ (Å)</th>
</tr>
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<tr>
<td>1</td>
<td>C$<em>6$H$</em>{10}$N$_2$</td>
<td>6.687 (11)</td>
<td>1.672</td>
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<tr>
<td>CIJZEB$^a$</td>
<td>C$_7$H$_4$ClN$_3$O$_2$</td>
<td>6.1372 (5)</td>
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<tr>
<td>CIJZEB0$^b$</td>
<td>C$_7$H$_4$ClN$_3$O$_2$</td>
<td>6.3050 (10)</td>
<td>1.5763</td>
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<tr>
<td>EqEUNL$^c$</td>
<td>C$_8$H$_7$BF$_3$N$_2$</td>
<td>6.635 (3)</td>
<td>1.659</td>
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<tr>
<td>FIFRAN$^d$</td>
<td>C$_7$H$_7$N$_2$O$_2$</td>
<td>6.388 (2)</td>
<td>1.597</td>
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<tr>
<td>MURANT$^e$</td>
<td>C$_8$H$_7$N$_2$O$_2$</td>
<td>6.36 (2)</td>
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<tr>
<td>QOXVII$^f$</td>
<td>C$_7$H$_8$N$_2$O$_2$</td>
<td>6.5670 (7)</td>
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<tr>
<td>VORDIR$^g$</td>
<td>C$_7$H$_6$BF$_3$N$_2$</td>
<td>6.4865 (4)</td>
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<td>WIOLO$^h$</td>
<td>C$_6$H$_7$N$_2$O</td>
<td>6.722 (4)</td>
<td>1.681</td>
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</table>

References: (a) Kubicki & Wagner (2007a); (b) Kubicki & Wagner (2007b); (c) Takao & Ikeda (2008); (d) Rybalova et al. (1998); (e) Bryden (1957); (f) Nawrot et al. (2001); (g) Konstantinova et al. (2014); (h) Aldabbagh et al. (1999).

3. Database survey
For all database searches, version 5.42 of the CSD (Groom et al., 2016), including all updates until September 2021 were used. The examples compiled in Table 3 were restricted to entries with space group $Pnma$ crystallizing in unit cells similar to 1, with a tolerance of 0.7 Å for each unit-cell parameter.
These conditions were met by seventeen entries; eight of these show a packing analogous to that of 1.

4. Synthesis and crystallization
The target compound 1,3,5-trimethyl-1H-pyrazole (1) is readily available by the Knorr pyrazole synthesis using

Figure 3
Short methyl C—H⋯π contacts about a center of inversion in 1 shown as
dashed lines (Spek, 2020): $d(Cg⋯H^0) = 2.586$ Å; $\angle(C^a⋯H^b⋯Cg) = 140.97^\circ$. Symmetry code: ($b$) 1 − x, −y, 1 − z.

Figure 4
Hirshfeld surface (Turner et al., 2017) about one 1,3,5-trimethyl-1H-
pyrazole moiety in 1.

Figure 5
View of the unit cell of 1 along c (Spek, 2020), methyl groups omitted. The radii of the atoms essentially denote their van der Waals radii ($r_{vdW}$).
Table 4

Experimental details.

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<th>Crystal data</th>
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<tr>
<td>Chemical formula</td>
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<tr>
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<tr>
<td>Temperature (K)</td>
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<tr>
<td>V (Å³)</td>
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<tr>
<td>a, b, c (Å)</td>
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<td>µ (mm⁻¹)</td>
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<td>Crystal size (mm)</td>
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Data collection

<table>
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<th>Bruker APEX CCD</th>
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<td>Multi-scan (SADABS, Krause et al., 2015)</td>
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<td>Rint</td>
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</tbody>
</table>

Refinement

\[ R[F² > 2σ(F²)], wR(F²), S \] 0.047, 0.119, 0.87

No. of reflections 648

No. of parameters 50

H-atom treatment H-atom parameters constrained

ΔUₜₘₐₓ, ΔUₚₚₐₙₐₓ (e Å⁻³) 0.26, −0.23

Computer programs: SMART (Bruker, 2001), SAINT-Plus (Bruker, 2009), SHELXT2014/5 (Sheldrick, 2015), SHELX2015/2 (Sheldrick, 2015b), PLATON (Spek, 2020) and Mercury (Macrae et al., 2020).

6. Conclusion and outlook

What else can we learn from the packing of the simple heterocycle 1 in space group Pnma. Space filling is unexceptional; according to the well-known Kemptser–Lipson rule (Kemptser & Lipson, 1972) a molecule with eight non-hydrogen atoms should be associated with a residue volume of approximately 150 Å³. The unit cell of 1 will therefore contain four pyrazole molecules, necessarily in special positions. Wyckoff positions 4a and 4b require 1 symmetry and can be excluded whereas 4c appears compatible with the molecular symmetry. Harker vectors are subtended by atoms related by crystallographic symmetry. All Harker peaks and all Patterson cross peaks (Glusker et al., 1994; Viterbo, 2002) derived for occupied 4c positions should be characterized by a Patterson coordinate of 0.0 or 0.5 in the [010] direction. The Patterson function for 1 perfectly matches this expectation: The highest Patterson peak with a φ coordinate unequal to 0.0 or 0.5 has an intensity of less than 5% of the trivial origin peak. Our tri-methylpyrazole represents a well-suited example for teaching basic concepts of crystallography such as space groups, Wyckoff positions, packing rules, and popular short contacts!

Acknowledgements

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References


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1,3,5-Trimethyl-1H-pyrazole

Crystal data

C₆H₁₀N₂
Mr = 110.16
Orthorhombic, Pnma
a = 11.205 (19) Å
b = 6.687 (11) Å
c = 8.373 (15) Å
V = 627.3 (19) Å³
Z = 4
F(000) = 240

Dₐ = 1.166 Mg m⁻³
Mo Ka radiation, λ = 0.71073 Å
Cell parameters from 263 reflections
θ = 3.0°–19.7°
µ = 0.07 mm⁻¹
T = 100 K
Block, colorless
0.21 × 0.10 × 0.09 mm

Data collection

Bruker APEX CCD diffractometer
Radiation source: microsource
Multilayer optics monochromator
ω scans
Absorption correction: multi-scan
(SADABS; Krause et al., 2015)
Tmin = 0.657, T max = 0.745

6665 measured reflections
648 independent reflections
366 reflections with I > 2σ(I)
Rint = 0.138
θ max = 25.9°, θ min = 3.0°
h = −13→13
k = −8→8
l = −10→10

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.047
wR(F²) = 0.119
S = 0.87
648 reflections
50 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed

H-atom parameters constrained

w = 1/[σ²(Fo²) + (0.0645P)²]
where P = (Fo² + 2Fc²)/3
(Δ/σ) max < 0.001
Δρ max = 0.26 e Å⁻³
Δρ min = −0.23 e Å⁻³

Extinction correction: SHELXL-2019/2
(Sheldrick 2015b),
Fc*=kFc[1+0.001xFc²sin(2θ)]¹/⁴
Extinction coefficient: 0.011 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

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<th>z</th>
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Atomic displacement parameters (Å²)

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<th></th>
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<th>U¹²</th>
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<td>0.0177 (15)</td>
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<td>C3</td>
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<td>0.0033 (17)</td>
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</table>

Geometric parameters (Å, °)

|     | C4—H4A | C5—H5A | C5—H5B | C4—H4B | C4—H4B' | N1—N2 | N2—C1 | N2—C4 | C1—C2 | C1—C5 | C2—C3 | C2—H2 | C3—C6 | C3—N1—N2 | C1—N2—C4 | N1—N2—C4 | C1—C5—H5B | C4—H4B—C4—H4B' |
|-----|--------|--------|--------|--------|--------|-------|-------|-------|-------|-------|-------|-------|-------|--------|----------|----------|-----------|-----------------|-----------------|
| N1—C3 | 1.336 (4) | C4—H4A | 0.9800 | C4—H4B | 0.9800 | N1—N2 | 1.358 (4) | C4—H4B | 0.9800 | N2—C1 | 1.351 (4) | C4—H4B' | 0.9800 | N2—C4 | 1.448 (4) | C5—H5A | 0.9800 | C1—C2 | 1.360 (5) | C5—H5B | 0.9800 | C1—C5 | 1.478 (4) | C5—H5B' | 0.9800 | C2—C3 | 1.392 (4) | C6—H6A | 0.9800 | C2—H2 | 0.9500 | C6—H6B | 0.9800 | C3—C6 | 1.498 (5) | C6—H6B' | 0.9800 |
| C3—N1—N2 | 104.2 (3) | N2—C4—H4B' | 109.47 (10) | N2—C4—H4B' | 109.5 | C1—N2—C4 | 112.7 (2) | H4A—C4—H4B' | 109.5 | C1—N2—C4 | 127.3 (3) | H4B—C4—H4B' | 109.5 | N1—N2—C4 | 120.0 (3) | C1—C5—H5A | 109.5 | N1—N2—C4 | 105.8 (3) | C1—C5—H5B | 109.5 |
supporting information

N2—C1—C5 122.0 (3)  H5A—C5—H5B 109.5
C2—C1—C5 132.2 (3)  C1—C5—H5B' 109.47 (11)
C1—C2—C3 106.6 (3)  H5A—C5—H5B 109.5
C1—C2—H2 126.7  H5B—C5—H5B' 109.5
C2—C1—C5 132.2 (3)  C1—C5—H5B i 109.47 (11)
C1—C2—H2 126.7  C3—C6—H6A 109.5
C3—C2—H2 126.7  C3—C6—H6B 109.5
N1—C3—C2 110.8 (3)  C3—C6—H6Bi 109.47 (10)
N1—C3—C6 119.9 (3)  H6A—C6—H6B 109.5
C2—C3—C6 129.4 (3)  C3—C6—H6B' 109.47 (10)
N2—C4—H4A 109.5  H6A—C6—H6B 109.5
N2—C4—H4B 109.5  H6B—C6—H6B' 109.5
H4A—C4—H4B 109.5

Symmetry code: (i) x, −y+1/2, z.

Comparison of selected distances in 1 with two comparable structures.
For PYRZOL27 a Z' of 2 is observed and only values for the first residue have been taken into account.

<table>
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<tr>
<th>Compound</th>
<th>d(N—N)</th>
<th>d1(N═C)</th>
<th>d2(N═C)</th>
<th>d1(C═C)</th>
<th>d2(CC)</th>
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<tbody>
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<td>1</td>
<td>1.358 (4)</td>
<td>1.351 (4)</td>
<td>1.336 (4)</td>
<td>1.392 (4)</td>
<td>1.360 (5)</td>
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<tr>
<td>PYRZOL27</td>
<td>1.357 (2)</td>
<td>1.338 (3)</td>
<td>1.334 (3)</td>
<td>1.391 (3)</td>
<td>1.373 (3)</td>
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<tr>
<td>ALOSEZ</td>
<td>1.3464 (17)</td>
<td>1.3595 (14)</td>
<td>1.3415 (16)</td>
<td>1.3966 (15)</td>
<td>1.377 (2)</td>
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