Trimethylpyrazole: a simple heterocycle reflecting Kitaigorodskii’s packing principle

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The five-membered heterocycle 1,3,5-trimethyl-1H-pyrazole, C₆H₁₀N₂ (1) 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 1 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 (1) in space...
group Pnma and describe its crystal packing in the context of Kitaigorodskii’s and Wilson’s ideas.

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 Pnma2 and Pbcn; Sikora & Kratusiak, 2013), 3,5-dimethyl-1H-pyrazole (space group R̅3c; 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 as most of them do not crystallize in space groups exhibiting a mirror plane, e.g. 1H-pyrazole (space groups Pnma2 and Pbcn; Sikora & Kratusiak, 2013), 3,5-dimethyl-1H-pyrazole (space group R̅3c; 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).



References: (a) Sikora & Kratusiak (2013); (b) Schmidt et al. (2003).
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 H4b⋯N2a [symmetry code: (a) 1 − x, −1/2 + y, 1 − z] = 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 \( d_{\text{norm}} \); red areas indicate short contacts. Both the C⋯H⋯N hydrogen bond and the interlayer methyl⋯π 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 (\( r_{\text{vdW}} \)) of 1.8 Å for carbon and of 1.58 Å for nitrogen (Kitaigorodskii, 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 matching the expected fourfold van der Waals radius of the non-hydrogen atoms involved. Table 3 shows additional examples for small and planar organic molecules crystallizing in the same space group type and with a similar cell parameter \( b \).

These examples share the same construction principle: The individual flat molecules are arranged in the crystallographic mirror plane, and for symmetry reasons dipole directions alternate between consecutive layers along \( b \).

### 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](image3.png)

Short methyl C−H⋯π contacts about a center of inversion in \( 1 \) shown as dashed lines (Speck, 2020): \( d(Cg - H^2) = 2.586 \text{ Å}; \angle(C^6 - H^4 - Cg) = 140.97^\circ \). Symmetry code: (b) \( 1 - x, -y, 1 - z \).

**Figure 3**

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

**Figure 4**

**Table 3**

| Compound | Formula | \( b \) (Å) | \( b/4 \) (Å) |
|----------|---------|-------------|-------------|
| 1        | \( \text{C}_6\text{H}_7\text{N}_2 \) | 6.687 (11) | 1.672 |
| CIJZEB\(^a\) | \( \text{C}_4\text{H}_6\text{ClN}_3\text{O}_2 \) | 6.1372 (5) | 1.5343 |
| CIJZEB0\(^b\) | \( \text{C}_4\text{H}_6\text{ClN}_3\text{O}_2 \) | 6.3050 (10) | 1.5763 |
| EQENU\(^c\) | \( \text{C}_9\text{H}_{16}\text{BF}_3\text{N}_2 \) | 6.635 (3) | 1.659 |
| FIFRAN\(^d\) | \( \text{C}_7\text{H}_8\text{N}_2\text{O}_2 \) | 6.388 (2) | 1.597 |
| MURANT\(^e\) | \( \text{C}_7\text{H}_8\text{N}_2\text{O}_2 \) | 3.63 (2) | 1.59 |
| OQN\(^f\) | \( \text{C}_7\text{H}_8\text{N}_2\text{O}_2 \) | 6.5670 (7) | 1.6418 |
| VORDIR\(^g\) | \( \text{C}_6\text{H}_5\text{OS} \) | 6.4865 (4) | 1.6216 |
| WIQL\(^h\) | \( \text{C}_6\text{H}_10\text{N}_2 \) | 6.722 (4) | 1.681 |

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).

![Figure 5](image5.png)

View of the unit cell of \( 1 \) along \( c \) (Speck, 2020), methyl groups omitted. The radii of the atoms essentially denote their van der Waals radii (\( r_{\text{vdW}} \)).
Table 4
Experimental details.

| Crystal data          | Chemical formula | C\textsubscript{6}H\textsubscript{10}N\textsubscript{2} |
|-----------------------|------------------|----------------------------------|
| M\textsubscript{r}    | 110.16           |                                  |
| Crystal system, space group | Orthorhombic, Pnma |                                |
| Temperature (K)        | 100              |                                  |
| a, b, c (Å)            | 11.205 (19), 6.687 (11), 8.373 (15) |                        |
| V (Å\textsuperscript{3}) | 627.3 (19)      |                                  |
| Z                      | 4                |                                  |
| Data collection        | Refinement       |                                  |
| Diffractometer         | Bruker APEX CCD  |                                  |
| Absorption correction  | Multi-scan (SADABS, Krause et al., 2015) |                          |
| T\textsubscript{min}, T\textsubscript{max} | 0.657, 0.745 |                                |
| No. of measured, independent and observed [I > 2\sigma(I)] reflections | 6665, 648, 366 |                                |
| R\textsubscript{int}  | 0.138            |                                  |
| No. of reflections     | 648              |                                  |
| No. of parameters      | 50               |                                  |
| H-atom treatment      | H-atom parameters constrained |                                  |
| ΔU\textsubscript{max}, ΔU\textsubscript{pmax} (e Å\textsuperscript{-3}) | 0.26, -0.23 |                                  |

Computer programs: SMART (Bruker, 2001), SAINT-Plus (Bruker, 2009), SHELXTL2014/5 (Sheldrick, 2015a), SHELXL2015/2 (Sheldrick, 2015b), PLATON (Spek, 2020) and Mercury (Macrae et al., 2020).

5. Refinement details

Crystal data, data collection parameters and convergence results for the single crystal X-ray diffraction experiment have been summarized in Table 4. Non-hydrogen atoms were assigned anisotropic displacement parameters. H atoms were introduced into calculated positions and treated as riding with C—H = 0.98 Å and U\textsubscript{iso}(H) = 1.5U\textsubscript{eq}(C) for methyl and with C—H = 0.95 Å and U\textsubscript{iso}(H) = 1.2U\textsubscript{eq}(C) for the heteroaryl H atom. Tentative refinement of a model in which the methyl conformations were chosen to best match local difference-Fourier maxima leads to split positions, but for each CH\textsubscript{3} group one H atom is located very close to the crystallographic mirror plane. We therefore decided to constrain the y coordinate of these almost in-plane hydrogens to fit the special position.

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 (Kempster & Lipson, 1972) a molecule with eight non-hydrogen atoms should be associated with a residue volume of approximately 150 Å\textsuperscript{3}. The unit cell of 1 will therefore contain four pyrazole molecules, necessarily in special positions. Wyckoff positions 4a and 4b require T 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 \(v\) coordinate unequal to 0.0 or 0.5 has an intensity of less than 5% of the trivial origin peak. Our trimethylpyrazole represents a well-suited example for teaching basic concepts of crystallography such as space groups, Wyckoff positions, packing rules, and popular short contacts!

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Computing details

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2009); data reduction: SAINT-Plus (Bruker, 2009); program(s) used to solve structure: SHELXT2014/5 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2019/2 (Sheldrick, 2015b); molecular graphics: PLATON (Spek, 2020) and Mercury (Macrae et al., 2020).

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  

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, Tmax = 0.745  
648 independent reflections  
64886 measured reflections  
h = −13 to 13  
k = −8 to 8  
l = −10 to 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  
Δρmax = 0.26 e Å⁻³  
Δρmin = −0.23 e Å⁻³  
Extinction correction: SHELXL-2019/2 (Sheldrick 2015b),  
Fc = kFc[1+0.001xFc²/σ²(2θ)]¹/⁴  
Extinction coefficient: 0.011 (4)

Mo Kα 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  

Δρmax = 0.26 e Å⁻³  
Δρmin = −0.23 e Å⁻³  
Extinction correction: SHELXL-2019/2 (Sheldrick 2015b),  
Fc = kFc[1+0.001xFc²/σ²(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)**

|    | x      | y      | z      | U₁₁    | U₂₂    | U₃₃    | U₁₂    | U₁₃    | U₂₃    |
|----|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| N1 | 0.4912 (2) | 0.250000 | 0.6988 (3) | 0.0289 (7) |       |       |       |        |        |
| N2 | 0.5279 (2) | 0.250000 | 0.5442 (3) | 0.0249 (6) |       |       |       |        |        |
| C1 | 0.6481 (3) | 0.250000 | 0.5301 (4) | 0.0236 (7) |       |       |       |        |        |
| C2 | 0.6912 (3) | 0.250000 | 0.6820 (3) | 0.0260 (8) |       |       |       |        |        |
| H2 | 0.772711 | 0.250000 | 0.713077 | 0.031* |       |       |       |        |        |
| C3 | 0.5924 (3) | 0.250000 | 0.7829 (4) | 0.0265 (7) |       |       |       |        |        |
| C4 | 0.4409 (3) | 0.250000 | 0.4164 (3) | 0.0327 (9) |       |       |       |        |        |
| H4A | 0.360267 | 0.250000 | 0.461847 | 0.049* |       |       |       |        |        |
| H4B | 0.451701 | 0.130335 | 0.350369 | 0.049* |       |       |       |        |        |
| C5 | 0.7079 (3) | 0.250000 | 0.3728 (4) | 0.0342 (8) |       |       |       |        |        |
| H5A | 0.794608 | 0.250000 | 0.388049 | 0.051* |       |       |       |        |        |
| H5B | 0.684366 | 0.369665 | 0.312985 | 0.051* |       |       |       |        |        |
| C6 | 0.5878 (3) | 0.250000 | 0.9617 (4) | 0.0380 (9) |       |       |       |        |        |
| H6A | 0.504403 | 0.250000 | 0.996905 | 0.057* |       |       |       |        |        |
| H6B | 0.628021 | 0.369665 | 1.002625 | 0.057* |       |       |       |        |        |

**Atomic displacement parameters (Å²)**

|    | U₁₁    | U₂₂    | U₃₃    | U₁₂    | U₁₃    | U₂₃    |
|----|--------|--------|--------|--------|--------|--------|
| N1 | 0.0378 (16) | 0.0195 (13) | 0.0295 (16) | 0.000 | 0.0012 (14) | 0.000 |
| N2 | 0.0297 (15) | 0.0182 (13) | 0.0268 (15) | 0.000 | −0.0012 (12) | 0.000 |
| C1 | 0.0238 (16) | 0.0149 (15) | 0.032 (2) | 0.000 | 0.0009 (14) | 0.000 |
| C2 | 0.0263 (17) | 0.0177 (15) | 0.034 (2) | 0.000 | −0.0025 (16) | 0.000 |
| C3 | 0.0356 (17) | 0.0166 (14) | 0.0274 (18) | 0.000 | −0.0035 (17) | 0.000 |
| C4 | 0.038 (2) | 0.0228 (15) | 0.037 (2) | 0.000 | −0.0104 (16) | 0.000 |
| C5 | 0.040 (2) | 0.0275 (16) | 0.035 (2) | 0.000 | 0.0047 (16) | 0.000 |
| C6 | 0.048 (2) | 0.0349 (17) | 0.031 (2) | 0.000 | 0.0033 (17) | 0.000 |

**Geometric parameters (Å, º)**

|    |        |        |        |        |        |        |
|----|--------|--------|--------|--------|--------|--------|
| N1—C3 | 1.336 (4) | C4—H4A | 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 |        |        |        |
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.

| Compound     | d(N—N)    | d1(N═C)   | d2(N═C)   | d1(C═C)   | d2(CC)   |
|--------------|-----------|-----------|-----------|-----------|----------|
| 1            | 1.358 (4) | 1.351 (4) | 1.336 (4) | 1.392 (4) | 1.360 (5) |
| PYRZOL27     | 1.357 (2) | 1.338 (3) | 1.334 (3) | 1.391 (3) | 1.373 (3) |
| ALOSEZ       | 1.3464 (17)| 1.3595 (14)| 1.3415 (16)| 1.3966 (15)| 1.377 (2) |

Symmetry code: (i) x, −y+1/2, z.