

2,6-Dimethylpyrazine at 5 K: a neutron-diffraction study

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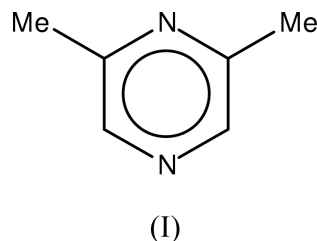
Key indicators

Single-crystal neutron study
 $T = 5$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.032
 wR factor = 0.016
Data-to-parameter ratio = 7.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Single-crystal neutron-diffraction techniques are used to determine the crystal structure of 2,6-dimethylpyrazine (DMP), $\text{C}_6\text{H}_8\text{N}_2$, at 5 K. The space group is $P2_1/a$ with $Z = 4$, as at room temperature. The methyl groups are ordered. There are two crystallographically inequivalent methyl groups in the unit cell. Different rotational dynamics may account for the two rotational tunnelling transitions observed with inelastic neutron-scattering techniques.

Comment

As found for the structure of this material, (I), at 20 K (Kaiser-Morris *et al.*, 2001), the space group is $P2_1/a$ (monoclinic) with four molecules per unit cell. There is no evidence for any phase transition between 20 and 5 K, and no significant changes of the lattice parameters below 20 K.



The structure consists of parallel layers of planar molecules perpendicular to the $(\bar{2}01)$ plane (Kaiser-Morris *et al.*, 2001). The protons of the methyl groups are quite localized at all temperatures. For each methyl group, one of the protons is almost in the molecular plane. The displacement ellipsoids for both methyl groups correspond quite well to those anticipated for hindered rotors with a rather high potential barrier and threefold symmetry (Fig. 1). There are two different crystallographic environments for the methyl groups linked to the same pyrazine ring. The different local potentials may account for the different tunnelling frequencies. This is confirmed by further inelastic neutron-scattering measurements performed on single crystals (Nicolai *et al.*, 1998).

Experimental

2,6-Dimethylpyrazine (DMP) is hygroscopic and melts at 311 K. We performed neutron-diffraction experiments with a single crystal at 5 K on the four-circle neutron diffractometer 5-C2 at the LLB (Saclay, France). A large single crystal ($1 \times 1 \times 5$ cm) was obtained at low temperature. A small single crystal ($5 \times 5 \times 5$ mm) was cut, glued on a goniometer head and oriented on 5-C2. The measurements were performed with the ω scan mode and an incident wavelength close to 0.83 Å selected with the Cu (220) monochromator.

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Crystal data

$C_6H_8N_2$
 $M_r = 108.14$
 Monoclinic, $P2_1/a$
 $a = 7.287$ (7) Å
 $b = 10.725$ (9) Å
 $c = 7.452$ (8) Å
 $\beta = 90.37$ (9)°
 $V = 582.4$ Å³
 $Z = 4$
 $D_x = 1.23$ Mg m⁻³

Data collection

Orphée reactor (Saclay, France):
 5-C2 four-circle
 ω scans
 Absorption correction: none
 2026 measured reflections
 1605 independent reflections
 1153 reflections with $I > 3\sigma(I)$
 $R_{int} = 0.022$

Refinement

Refinement on F
 $R = 0.032$
 $wR = 0.016$
 $S = 1.04$
 1153 reflections
 146 parameters
 All H-atom parameters refined
 Weighting scheme: Chebyshev
 polynomial with 5 parameters:
 0.951, -3.12, 0.00654, -0.885,
 -0.649 (Carruthers & Watkin,
 1979)

Neutron radiation
 $\lambda = 0.8308$ Å
 Cell parameters from 16
 reflections
 $\theta = 9.8$ – 21.5°
 $\mu = 0.08$ mm⁻¹
 $T = 5$ K
 Prism, white
 $5.0 \times 5.0 \times 5.0$ mm

$\theta_{max} = 35^\circ$
 $h = -10 \rightarrow 10$
 $k = -14 \rightarrow 4$
 $l = -10 \rightarrow 4$
 2 standard reflections
 frequency: 450 min
 intensity decay: none

$(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.78$ e Å⁻³
 $\Delta\rho_{min} = -0.73$ e Å⁻³
 Extinction correction: Larson
 (1970)
 Extinction coefficient: 2.39 (18)
 Atomic scattering factors from
 Sears (1992)

Table 1

Selected geometric parameters (Å, °).

N1–C1	1.3341 (11)	C1–C2	1.4023 (12)
N1–C4	1.3397 (11)	C2–C5	1.4991 (13)
N2–C2	1.340 (1)	C3–C4	1.3982 (13)
N2–C3	1.3394 (11)	C3–C6	1.4980 (12)
C1–N1–C4	116.27 (7)	C1–C2–C5	120.37 (8)
C2–N2–C3	117.44 (7)	N2–C3–C4	120.71 (8)
N1–C1–C2	122.04 (8)	N2–C3–C6	117.74 (8)
N2–C2–C1	121.07 (8)	C4–C3–C6	121.55 (8)
N2–C2–C5	118.56 (8)	N1–C4–C3	122.47 (8)

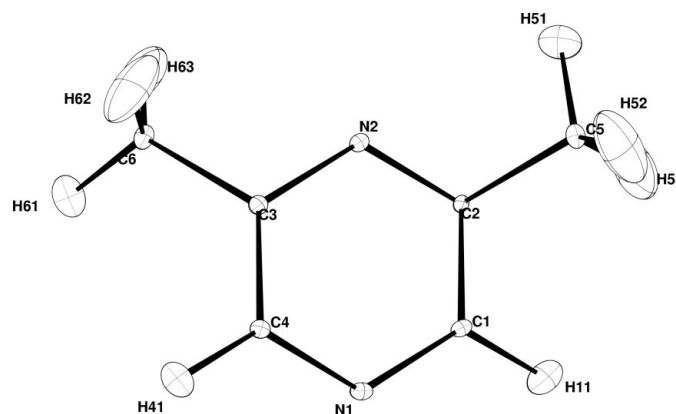


Figure 1

The molecular structure of (I) at 5 K, with 50% probability displacement ellipsoids. For a packing diagram, see the preceding paper (Kaiser-Morris *et al.*, 2001).

Data collection: *DIF4N* (modified Linux version of *DIF4*; Stoe & Cie; 2000); cell refinement: *DIF4N*; data reduction: *PRON* (modified version of *REDU4*; Stoe & Cie, 2000); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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