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# 2,6-Dimethylpyrazine at 20 K: a neutron-diffraction study

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**Key indicators**

Single-crystal neutron study
$T$ = 20 K
Mean $\sigma$(C–C) = 0.002 Å
$R$ factor = 0.031
$wR$ factor = 0.019
Data-to-parameter ratio = 9.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.



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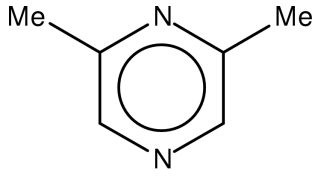
Single crystal neutron diffraction techniques are used to determine the crystal structure of 2,6-dimethylpyrazine (DMP), $C_6H_8N_2$, at 20 K. The space group is $P2_1/a$ with $Z$ = 4, as at room temperature. The methyl groups are ordered. There are two crystallographically inequivalent methyl groups in the unit cell.

## Comment

Light particles experiencing potential functions with topological degeneracy manifest their quantum nature *via* tunnelling. The magnitude of the tunnel splitting depends on the particle mass and potential shape (distances between identical sites and barrier height). For methyl groups the threefold symmetry ensures strict topological degeneracy and rotational tunnelling has been observed with inelastic neutron-scattering techniques (INS) in many crystals (Press, 1981; Prager & Heidemann, 1995). The INS spectrum of DMP at 2 K exhibits tunnelling lines at 20 and 29 μeV (Nicolaï, Kaiser *et al.*, 1998). The presence of more than one tunnelling transition in the same system is rather rare. It reveals either inequivalent methyl groups or dynamical coupling. A precise knowledge of the crystalline structure at the same temperature of the tunnelling measurements is necessary to interpret the INS spectra (Johnson *et al.*, 1996; Johnson *et al.*, 1997; Neumann & Johnson, 1997; Nicolaï, Kearley *et al.*, 1998). We present in this paper the structure determination at 20 K. The structure at the temperature of the tunnelling experiment, 5 K, is presented in the following article (Kaiser-Morris *et al.*, 2001).




(I)

The space group $P2_1/a$ (monoclinic) with four formula units per unit cell was obtained from a preliminary study at 253 K with X-rays (Morris *et al.*, 1998) and a recent X-ray diffraction study at 180 K with a better resolution (Thalladi *et al.*, 2000). A preliminary neutron-diffraction experiment at 260 K, close to the melting point of the title compound, and neutron-diffraction experiments on a single crystal at 20 and 5 K confirmed the space group $P2_1/a$ (Fig. 1). There is no evidence for any phase transition between 260 and 20 K, but there are significant changes of the lattice parameters below 260 K: at

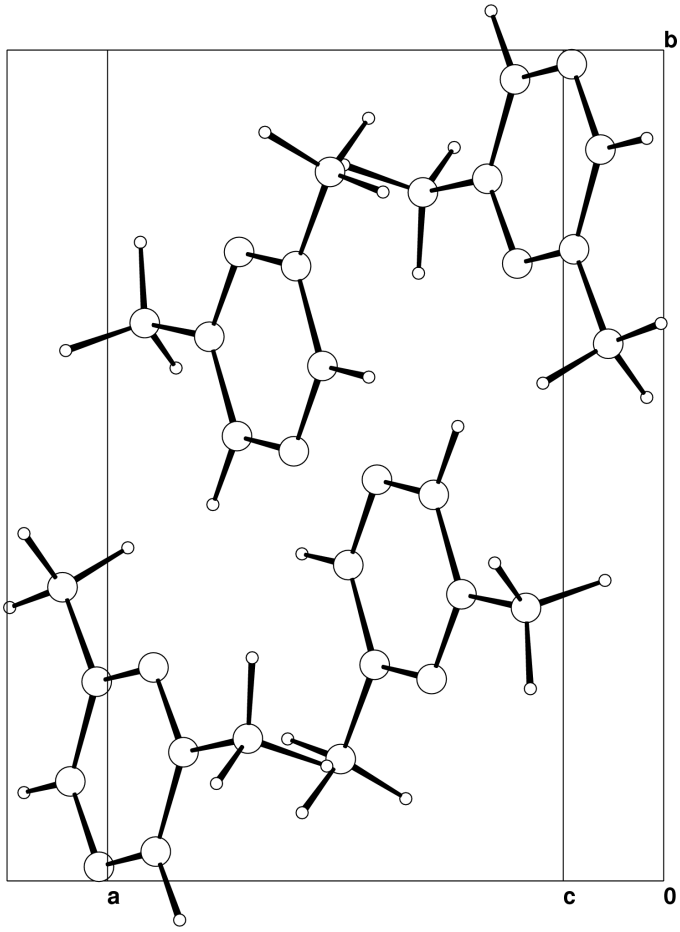



**Figure 1**
The crystal structure of (I) at 20 K. For a single-molecule representation, see the following paper (Kaiser-Morris *et al.*, 2001).

260 K, the cell parameters are: $a$ = 7.467 (8), $b$ = 10.859 (7), $c$ = 7.558 (7) Å, $\beta$ = 90.8 (4)°.

## Experimental

2,6–Dimethylpyrazine (DMP) is hygroscopic and melts at 311 K. We performed neutron-diffraction experiments with a single crystal at 260, 20 and 5 K on the four-circle neutron diffractometer 5-C2 at the LLB (Saclay, France). A large single crystal (1 × 1 × 5 cm) was obtained at low temperature. A small single crystal (5 × 5 × 5 mm) was cut, glued on a goniometer head and oriented on 5-C2. The measurements were performed with the $\omega$ scan mode and an incident wavelength close to 0.83 Å selected with the Cu (220) monochromator.

*Crystal data*

$C_6H_8N_2$
$M_r$ = 108.14
Monoclinic, $P2_1/a$
$a$ = 7.288 (5) Å
$b$ = 10.73 (1) Å
$c$ = 7.444 (7) Å
$\beta$ = 90.10 (8)°
$V$ = 582.4 Å$^3$
$Z$ = 4
$D_x$ = 1.23 Mg m$^{-3}$
Neutron radiation
$\lambda$ = 0.8308 Å
Cell parameters from 16 reflections
$\theta$ = 9.8–21.5°
$\mu$ = 0.08 mm$^{-1}$
$T$ = 20 K
Prism, white
5.0 × 5.0 × 5.0 mm

*Data collection*

Orphée reactor (Saclay, France): 5-C2 four-circle
$\omega$ scans
Absorption correction: none
2230 measured reflections
1918 independent reflections
1337 reflections with $I > 3\sigma(I)$
$R_{int}$ = 0.074
$\theta_{max}$ = 37.5°
$h = -10 \rightarrow 2$
$k = 0 \rightarrow 15$
$l = -10 \rightarrow 10$
2 standard reflections
frequency: 450 min
intensity decay: none

*Refinement*

Refinement on $F$
$R$ = 0.031
$wR$ = 0.019
$S$ = 1.03
1337 reflections
146 parameters
All H-atom parameters refined
Weighting scheme: Chebychev polynomial with 5 parameters: 1.04, −3.06, −0.108, −0.644, −0.800 (Carruthers & Watkin, 1979)
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.83 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.89 e Å$^{-3}$
Extinction correction: Larson (1970)
Extinction coefficient: 1.52 (13)
Atomic scattering factors from Sears (1992)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| N1—C1 | 1.3354 (9) | C1—C2 | 1.4040 (11) |
| N1—C4 | 1.341 (1) | C2—C5 | 1.5005 (11) |
| N2—C2 | 1.3399 (9) | C3—C4 | 1.3960 (11) |
| N2—C3 | 1.340 (1) | C3—C6 | 1.5019 (11) |
| | | | |
| C1—N1—C4 | 116.19 (6) | C1—C2—C5 | 120.45 (7) |
| C2—N2—C3 | 117.47 (6) | N2—C3—C4 | 120.78 (7) |
| N1—C1—C2 | 122.06 (7) | N2—C3—C6 | 117.72 (7) |
| N2—C2—C1 | 120.99 (7) | C4—C3—C6 | 121.50 (7) |
| N2—C2—C5 | 118.56 (7) | N1—C4—C3 | 122.51 (7) |

Data collection: *DIF4N* (modified Linux version of *DIF*4; Stoe & Cie, 2000); cell refinement: *DIF4N*; data reduction: *PRON* (modified version of *REDU*4; 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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