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Tetramethylpyrazine at 300 and 100 K

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Abstract. $C_8H_{12}N_2$, orthorhombic, *Pbca*. At 300 K: $a = 8{\cdot}328\,(6)$, $b = 9{\cdot}270\,(5)$, $c = 10{\cdot}200\,(7)$ Å, $d_x = 1{\cdot}15$ Mg m^{-3}. At 100 K: $a = 8{\cdot}331\,(6)$, $b = 9{\cdot}225\,(5)$, $c = 10{\cdot}148\,(9)$ Å, $d_x = 1{\cdot}16$ Mg m^{-3}. The known structure was refined by full-matrix least-squares techniques to $R_w = 0{\cdot}084$ (821 reflections; 300 K) and $R_w = 0{\cdot}045$ (1835 reflections; 100 K).

Introduction. The structure of tetramethylpyrazine (TMP) has been determined and refined to $R = 0{\cdot}23$ by Cromer, Ihde & Ritter (1951). In connection with future force-field calculations on nitrogen-containing aromatic compounds more accurate values for the atomic positions in TMP are required. It was therefore decided to refine the structure at 300 and 100 K with new sets of intensities.

Crystallization of TMP by sublimation gives pyramidal crystals. During data collection sublimation of the crystals was prevented by covering them with a thin film of TIXO (a cyanoacrylate monomer glue which polymerizes rapidly in air). The crystals were mounted on the tip of a glass capillary to keep absorption by the glass as small as possible. Weissenberg photographs indicated the space group *Pbca* both at room temperature and at 100 K. Intensities and cell dimensions were measured on a Nonius CAD-3 diffractometer with Zr-filtered Mo radiation.

At 300 K a crystal 0·55 × 0·45 × 0·35 mm was used. The cell dimensions were adjusted to the optimized setting angles of 12 reflections by a least-squares procedure. Intensities were collected with the θ–2θ scan technique, a constant counter slit of 2·0 mm and scan angles varying according to $(0{\cdot}9 + 0{\cdot}8\,\mathrm{tg}\,\theta)^\circ$. Deviations from linearity of the counting equipment were kept below 1% by the use of attenuation filters. The intensities of reference reflections were constant within experimental error. In one run two sets of independent reflections were collected. Weighted averages of the intensities of equivalent reflections were calculated with the program *VMS* (written in our laboratory). The resulting set was corrected for Lorentz and polarization effects, and contains 1148 reflections among which 906 had $I > 0$.

The refinement at 300 K by full-matrix least-squares techniques was based on 821 reflections with $|F_o| > 2\sigma(F_o)$; the weighting scheme $w = [\sigma^2(F_o) + D|F_o| + E|F_o|^2 + G|F_o|^H]^{-1}$, with $\sigma(F_o)$ the standard deviation in F_o due to counting statistics, and $D = -0{\cdot}240$, $E = 0{\cdot}0267$, $G = 0{\cdot}485$ and $H = 3$, chosen such that deviations in $\langle w(|F_o| - |F_c|)^2\rangle$ as a function of $|F_o|$ were kept as small as possible. H atoms were found from difference syntheses and constrained at C—H = 1·08 Å. For the non-hydrogen atoms scattering curves were from Cromer & Mann (1968) and for H from

Table 1. *Fractional atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

For numbering scheme, see Fig. 1. The first digit of an H atom gives the number of the C atom to which it is connected.

	300 K			100 K (*w*)			100 K [*w*(*VMS*)]			100 K (corrected)*		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
C(1)	76 (3)	1388 (2)	329 (2)	66·7 (9)	1418·5 (8)	335·4 (8)	67·3 (11)	1418·8 (9)	336·5 (8)	67·9 (11)	1421·2 (9)	336·4 (8)
C(2)	−850 (3)	434 (2)	1037 (2)	−872·1 (8)	429·7 (8)	1055·4 (7)	−871·5 (11)	430·8 (9)	1054·4 (8)	−873·5 (11)	430·5 (9)	1056·8 (8)
C(3)	203 (4)	2951 (3)	693 (3)	152·7 (11)	2992·6 (9)	716·1 (9)	155·4 (13)	2994·0 (9)	715·1 (9)	156·0 (13)	2998·5 (9)	716·4 (9)
C(4)	−1815 (4)	899 (3)	2200 (3)	−1849·0 (11)	903·4 (10)	2232·3 (8)	−1849·5 (12)	902·0 (11)	2232·9 (9)	−1852·8 (12)	903·0 (11)	2236·6 (9)
N	918 (2)	958 (2)	−704 (2)	928·7 (8)	979·5 (7)	−714·0 (7)	929·4 (9)	980·0 (8)	−715·0 (7)	931·6 (9)	982·1 (8)	−716·0 (7)
H(31)	1104	3466	92	1016·8	3537·2	96·3	1019·5	3538·6	95·3	1021·1	3543·1	95·8
H(32)	533	3050	1711	517·8	3083·8	1733·8	520·5	3058·2	1732·8	521·1	3089·7	1733·3
H(33)	−961	3465	533	−1011·6	3488·3	590·4	−1008·9	3489·7	589·4	−1008·3	3494·2	556·9
H(41)	−1072	891	3077	−1054·7	1275·9	3002·1	−1055·2	1274·5	3002·7	−1058·5	1275·5	3007·0
H(42)	−2803	159	2330	−2547·1	−1·3	2589·8	−2547·6	−2·7	2590·4	−2550·9	−1·7	2594·7
H(43)	−2275	1974	2043	−2645·1	1772·9	1948·4	−2645·6	1771·5	1949·0	−2468·9	1772·5	1953·3

* Averaged coordinates corrected for librational effects.

Table 2. *Isotropic thermal parameters*

For H atoms the isotropic parameter U ($\times 10^3$) is presented; for non-hydrogen atoms U ($\times 10^4$) $= \frac{1}{3}\sum_i U_{ii}$, with U_{ii} the diagonal elements of a diagonalized anisotropic $\mathbf{U}$ matrix.

		100 K	100 K			100 K	100 K
	300 K	(*w*)	[*w*(*VMS*)]		300 K	(*w*)	[*w*(*VMS*)]
	U	*U*	*U*		*U*	*U*	*U*
C(1)	451 (6)	165 (2)	169 (2)	H(31)	140 (16)	56 (4)	52 (4)
C(2)	444 (6)	165 (2)	168 (2)	H(32)	108 (13)	48 (4)	51 (4)
C(3)	631 (9)	234 (2)	238 (2)	H(33)	125 (15)	50 (5)	48 (4)
C(4)	633 (9)	238 (2)	243 (2)	H(41)	148 (17)	57 (5)	53 (4)
N	474 (6)	177 (2)	181 (2)	H(42)	100 (12)	46 (4)	41 (3)
				H(43)	94 (11)	41 (4)	41 (4)

Stewart, Davidson & Simpson (1965). For H isotropic and for non-hydrogen atoms anisotropic thermal parameters were refined. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}084$, goodness of fit $G = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2} = 1{\cdot}09$ with $N_o = 821$ and $N_v = 52$. Final coordinates are given in Table 1.[*] Isotropic thermal parameters are in Table 2.

At 100 K an almost spherical crystal with $\varnothing = 0{\cdot}50$ mm was used for data collection. The crystal was cooled in a stream of cold nitrogen gas (van Bolhuis, 1971). In principle the same measuring technique as at room temperature was applied. This time the cell dimensions were obtained from 23 reflections and the scan angle was $(1{\cdot}0 + 0{\cdot}8\ \mathrm{tg}\ \theta)^\circ$. Corrections for the intensity changes deduced from reference reflections were $<3{\cdot}0\%$. Four series of equivalent reflections were measured up to $\theta = 40^\circ$. Their relative scale factors according to Hamilton, Rollett & Sparks (1965) and weighted average intensities $I_{\rm av}(\mathbf{H})$ were calculated with the program *VMS* and the weighting scheme $w(I) = [\sigma^2_{\rm count}(I) + CI^2]^{-1}$. For one series which seemed to be affected by instabilities in the measuring equipment $\sigma^2_{\rm count}$ was multiplied by 4. The constant C was found by least-squares adjustment of $\langle w^{-1}(I)\rangle$ to $\langle [I_i(\mathbf{H}) - I^p_{\rm av}(\mathbf{H})]^2\rangle$ for sets of reflections grouped according to I and taken from all measuring series $i = 1$–4; $I^p_{\rm av}(\mathbf{H})$ is the weighted average as calculated in the previous cycle. Alternating cycles of scaling and C refinement were applied until self-consistency was reached. Final scale factors for series 1, 2 and 3 are 0·9278 (18), 0·9572 (14) and 0·9477 (14) with respect to series 4, $C = 0{\cdot}30 \times 10^{-3}$ and $R_w = \{\sum_{\mathbf{H},i} w(\mathbf{H})\,[I_i(\mathbf{H}) - I_{\rm av}(\mathbf{H})]^2/\sum_{\mathbf{H},i} w(\mathbf{H}) I_i^2(\mathbf{H})\}^{1/2} = 0{\cdot}059$. The set of averaged intensities, which finally were corrected for Lorentz and polarization effects, contained 2394 reflections, among which 2111 had $I > 0$.

The refinement of the structure at 100 K was carried out in essentially the same way as at room temperature. 1835 reflections with $|F_o| > 2\sigma(F_o)$ were taken into account. In addition to a refinement with the normal weighting scheme $w = [\sigma_c^2(F_o) + E|F_o|^2]^{-1}$, a refinement with the scheme $w(VMS) = [\sigma_c^2(F_o) + E(VMS)|F_o|^2]^{-1}$ was performed. $\sigma_c^2(F_o)$ is calculated from the standard deviation in the average intensities due to counting statistics (including the factor 4 for one of the series); $E(VMS) = 0{\cdot}74 \times 10^{-4}$ was deduced from the C value found by *VMS*. Final agreement indices are $R(w) = 0{\cdot}065$, $G(w) = 1{\cdot}42$, $R(w\text{-}VMS) = 0{\cdot}045$ and $G(w\text{-}VMS) = 3{\cdot}19$.[*]

It is hard to judge which weighting scheme is better. $E(VMS)$ may be too low as it does not account for systematic errors common to all measuring series.

On the other hand, E may be too high as the neglect of bonding effects in the model affects particularly the F_c values of the low-order reflections which on average are relatively strong. Fortunately, the difference in weighting scheme hardly affects the final coordinates, as may be seen in Table 1. Further calculations were carried out with the average final parameters. A thermal-motion analysis with the program *TMA* (Shmueli, 1972) showed that the molecule can be described as a rigid body in good approximation. Coordinates corrected for libration are given in Table 1.

Discussion. The crystal structure of TMP is shown in Fig. 1. The four molecules in the cell lie at inversion

Table 3. *Geometric data with e.s.d.'s in parentheses*

For numbering scheme, see Fig. 1. The uncorrected data are based on the averaged coordinates of columns *w* and *w*(*VMS*) in Table 1.

(*a*) Bond lengths (Å) and angles (°)

		100 K	
	300 K	Uncorrected	Corrected
C(1)–C(3)	1·499 (3)	1·5045 (15)	1·5070 (15)
C(2)–C(4)	1·496 (4)	1·5104 (15)	1·5130 (15)
C(1)–C(2)	1·378 (3)	1·4054 (13)	1·4088 (13)
N–C(1)	1·327 (3)	1·3477 (14)	1·3500 (14)
N′–C(2)	1·336 (3)	1·3467 (14)	1·3491 (14)
C(3)–C(1)–C(2)	122·0 (2)	121·35 (9)	121·38 (9)
C(4)–C(2)–C(1)	122·1 (2)	121·57 (9)	121·60 (9)
C(3)–C(1)–N	116·8 (2)	117·83 (8)	117·78 (8)
C(4)–C(2)–N′[†]	117·2 (2)	117·55 (8)	117·50 (8)
C(2)–C(1)–N	121·3 (2)	120·82 (9)	120·84 (9)
C(1)–C(2)–N′	120·7 (2)	120·88 (9)	120·90 (9)
C(1)–N–C(2′)	118·0 (2)	118·31 (7)	118·26 (7)

(*b*) Largest deviations (Å) from the best plane of the ring

Ring atoms	0·0013 (4)	0·0007 (15)	0·0007 (15)
C(3)	0·0252 (4)	0·0138 (15)	0·0138 (15)
C(4)	0·0067 (4)	0·0028 (15)	0·0028 (15)

[†] A prime indicates an atom centrosymmetrically related to the atom in Table 1.

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[*] Lists of structure factors and thermal parameters obtained at both temperatures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35782 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[*] See previous footnote.

Table 4. *Mean bond lengths* (Å) *and angles* (°) *for TMP and related structures*

Values corrected for librational effects are given in parentheses. Atoms without special labels are ring atoms. E.s.d.'s are for average values.

	TMP (100 K)	Pyrazine (184 K)*	TMP (300 K)	TMP.3H_2O (300 K)†
C—C	1·4045 (1·4088)	1·3875 (1·3931)	1·378 (1·387)	1·381
C—N	1·3472 (1·3496)	1·3330 (1·3392)	1·331 (1·337)	1·332
C—C(H_3)	1·5074 (1·5100)		1·498 (1·504)	1·492
C—N—C	118·31 (118·26)	116·18 (116·31)	118·0 (117·9)	118·3
C—C—N	120·85 (120·87)	121·91 (121·84)	121·0 (121·1)	120·8
N—C—C(H_3)	117·69 (117·64)		117·0 (116·8)	117·3
C—C—C(H_3)	121·46 (121·49)		122·0 (122·1)	121·9
σ(length)	0·0006 (0·0006)	0·0006 (0·0006)	0·0014 (0·0014)	0·0012
σ(angle)	0·03 (0·03)	0·05 (0·05)	0·08 (0·08)	0·06

* De With, Harkema & Feil (1976).
† Braam, Eikelenboom, van Dijk & Vos (1981).

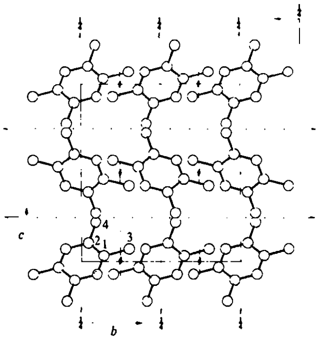

Fig. 1. Projection of the crystal structure along **a**. H atoms are not shown.

centres; only half the molecule is crystallographically independent. Geometric data based on the coordinates of Table 1 are presented in Table 3. The aromatic ring is planar within experimental error; one of the C(methyl) atoms shows a significant deviation from the plane of the ring.

The 300 K data in Table 4 show that the water molecules in TMP.3H_2O do not significantly affect the bond lengths and angles in the TMP molecules. Comparison with pyrazine, in which CH_3 is replaced by H, reveals that the presence of the CH_3 groups makes the C—N—C angles slightly larger and the C—C—N angles slightly smaller. In the future, the non-bonded interactions of the CH_3 groups with the rest of the molecule will be described more quantitatively by force-field calculations. The strain in the TMP molecule evidently also results in deviations of the C(methyl) atoms from the plane of the ring.

Comparison of the mean bond lengths in TMP and in related compounds (Table 4) shows that the bond lengths increase with decreasing temperatures. This well known effect is due to errors in the coordinates caused by neglect of librational and anharmonic parts of the thermal motion in the refinement model (Becka & Cruickshank, 1961). Even after application of libration corrections as calculated by the program *TMA* the bond lengths at room temperature are still too small, showing that at room temperature these libration corrections do not completely account for the errors in the coordinates. It is therefore possible that at low temperature also the corrected coordinates are still slightly incorrect. In force-field calculations uncertainties of this type can be reduced as much as possible, if in these calculations related structures at low and not-too-different temperatures are compared.

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