

Tetramethylpyrazine Trihydrate

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Abstract. $C_8H_{12}N_2 \cdot 3H_2O$, monoclinic, $P2_1/c$, $a = 7.003$ (8), $b = 13.385$ (12), $c = 11.640$ (15) Å, $\beta = 101.81$ (10)°, $D_x = 1.17$ Mg m⁻³, $Z = 4$. Final $R = 0.091$ for 1852 unique reflections. The two independent molecules have lower symmetry than expected for free tetramethylpyrazine.

Introduction. Crystallization from aqueous solution gives hydrated crystals of tetramethylpyrazine (TMP). In contradiction to TMP itself, for which pyramidal crystals were obtained (Braam, Eshuis & Vos, 1980; Cromer, Ihde & Ritter, 1951), the hydrated crystals have a needle-like shape. Easy dehydration prevents mounting of the crystals at room temperature. The crystals were therefore covered with a thin film of TIXO (a cyanoacrylate-monomer glue, which polymerizes rapidly in air) in a cold room (273–278 K), and then mounted on the tip of a glass capillary. Weissenberg photographs indicated the space group $P2_1/c$. Intensities and cell dimensions were measured at room temperature on a Nonius CAD-3 diffractometer with Zr-filtered Mo radiation for a crystal $0.45 \times 0.30 \times 0.30$ mm. The cell dimensions were adjusted to the setting angles of 12 reflections by least squares. Intensities were collected with a θ - 2θ scan, a counter slit of 2.0 mm and a scan angle of $(0.8 + 0.8 \text{tg } \theta)$ °. Deviations from linearity of the scintillation-counting equipment were kept below 1% by the use of attenuation filters. Corrections for changes in the primary-beam intensity as measured from intensity reference reflections were zero within experimental error. Two series of intensities both measured for the same hemisphere of reciprocal space up to 30° were compared and scaled according to Hamilton, Rollett & Sparks (1965) with the program *VMS* (written in our laboratory). The scale factor is 1.0493 (7) and $R_w = 0.029$. Weighted averages of equivalent reflections were corrected for Lorentz and polarization effects. The combined series contains 3133 reflections of which 2163 had $I > 0$.

An approximate structure model was obtained by direct methods. Normalized structure factors calculated by *NORMAL* on the basis of the complete molecules were used as input for *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson,

1978). The full-matrix least-squares refinement (XRAY system, 1976) was based on 1852 reflections with $|F_o| > 2\sigma(F_o)$; the weighting scheme $w = [\sigma^2(F_o) +$

Table 1. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^4$), with e.s.d.'s in parentheses

For H linked to C the first digit n in the number gives the C atom to which it is connected; for H linked to O this digit is replaced by O(n).

For hydrogen atoms the isotropic parameter U is presented; for non-hydrogen atoms $U = \frac{1}{3} \sum_i U_{ii}$, in which U_{ii} are the diagonal elements of a diagonalized anisotropic U matrix.

	x	y	z	U
Molecule A				
C(1)	3950 (4)	3054 (2)	4144 (2)	552 (9)
C(2)	4512 (3)	4075 (2)	4600 (2)	407 (7)
C(3)	4732 (3)	5745 (2)	4222 (2)	425 (8)
C(4)	4377 (5)	6577 (2)	3351 (3)	658 (11)
N(1)	4257 (3)	4823 (2)	3836 (2)	430 (7)
H(11)	2900	2731	4598	942 (110)
H(12)	3237	3032	3229	881 (107)
H(13)	5266	2615	4232	1221 (142)
H(41)	3238	7048	3554	1188 (144)
H(42)	4177	6301	2463	1053 (126)
H(43)	5665	7030	3387	1543 (186)
Molecule B				
C(5)	9004 (5)	9359 (3)	7636 (2)	703 (12)
C(6)	9506 (3)	9702 (2)	8885 (2)	460 (8)
C(7)	10637 (3)	9308 (2)	10817 (2)	447 (8)
C(8)	11365 (4)	8517 (2)	11700 (3)	607 (10)
N(2)	10135 (3)	9014 (2)	9695 (2)	475 (7)
H(51)	7548	9561	7188	1104 (133)
H(52)	9285	8571	7560	1245 (149)
H(53)	9775	9829	7130	1062 (126)
H(81)	8449	12198	8693	966 (116)
H(82)	9602	11544	7690	1228 (147)
H(83)	7295	11228	7744	1080 (129)
Water molecules				
O(1)	3636 (3)	4316 (2)	1347 (2)	619 (7)
O(2)	436 (3)	3115 (2)	756 (2)	735 (9)
O(3)	6838 (3)	4026 (2)	142 (2)	719 (12)
H(O11)	2639	3819	1188	1367 (169)
H(O12)	3696	4518	2139	1233 (152)
H(O21)	-824	3416	556	1765 (203)
H(O22)	149	2418	710	1133 (143)
H(O31)	5860	4096	599	1192 (144)
H(O32)	6806	4533	-438	903 (110)

$E|F_o|^{-2}]^{-1}$ with $\sigma(F_o)$ the e.s.d. in F_o due to counting statistics, and $E = 0.0025$ chosen such that variations in $\langle w(|F_o| - |F_c|)^2 \rangle$ as a function of $|F|$ were kept as small as possible. H atoms were found from difference syntheses and constrained at geometrically reasonable positions, C—H = 1.08, O—H = 0.95 Å. For the non-hydrogen atoms scattering curves were from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). For H isotropic, and for non-hydrogen atoms anisotropic thermal parameters were refined. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.091$, goodness of fit $G = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2} = 1.25$ with $N_o = 1852$ and $N_v = 136$. Final coordinates are given in Table 1.*

Analysis of the thermal vibrations of the non-hydrogen atoms with TMA (Shmueli, 1972) showed that the thermal motion of the TMP molecules can be described with a rigid-body model; $\langle (U_o - U_c)^2 \rangle$ is approximately equal to $\langle \sigma^2(U_o) \rangle$. Calculated libration corrections, which are of the order of the e.s.d.'s in the coordinates, were not applied because of the approximate nature of the rigid-body model.

Discussion. The crystal structure is shown in Fig. 1. Bond lengths and angles are presented in Table 2. The TMP molecules lie at inversion centres. There are two independent half molecules. The TMP molecules are connected by N...H—O hydrogen bridges to strings of water molecules along *a*. The strings contain the hydrogen bridges O(2)...H—O(1) = 2.729 (3), O(1)...H—O(3) = 2.794 (3) and O(3)...H—O(2) = 2.758 (3) Å. Neighbouring strings are connected *via* the TMP molecules by means of N(1)...H—O(1) = 2.920 (3) and N(2)...H—O(2) = 2.911 (3) Å and by O(1)...H—O(3) = 2.904 (3) Å.

For both molecules the aromatic rings are flat within experimental error; all deviations from the respective planes are < 0.0009 Å. Average values for the C—C = 1.381 Å and C—N = 1.332 Å bonds in the ring may be

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35607 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

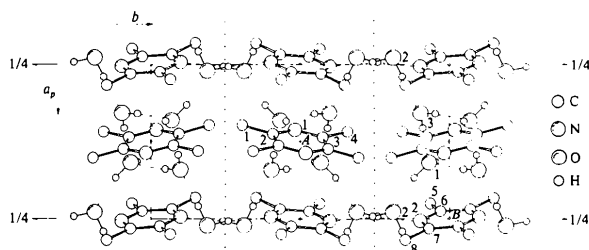


Fig. 1. Orthonormal projection of the crystal structure along *c*; *a_p* gives the projection of *a*. H atoms of CH₃ groups are not shown. Dashed lines indicate hydrogen bridges.

Table 2. Bond lengths (Å) and angles (°)

E.s.d.'s are given in parentheses. For the numbering scheme, see Fig. 1. *n'* indicates an atom centrosymmetrically related to *n*.

Molecule A		Molecule B	
C(1)—C(2)	1.490 (4)	C(5)—C(6)	1.496 (4)
C(3)—C(4)	1.492 (4)	C(7)—C(8)	1.491 (4)
N(1)—C(2)	1.327 (3)	N(2)—C(6)	1.327 (3)
N(1)—C(3)	1.333 (3)	N(2)—C(7)	1.340 (4)
C(2)—C(3')	1.386 (4)	C(6)—C(7')	1.378 (4)
C(1)—C(2)—C(3')	122.1 (2)	C(5)—C(6)—C(7')	121.7 (2)
C(2')—C(3)—C(4)	121.3 (2)	C(6')—C(7)—C(8)	122.7 (2)
N(1)—C(2)—C(1)	117.6 (2)	N(2)—C(6)—C(5)	117.1 (3)
N(1)—C(3)—C(4)	117.8 (2)	N(2)—C(7)—C(8)	116.6 (2)
N(1)—C(2)—C(3')	120.3 (2)	N(2)—C(6)—C(7')	121.3 (2)
N(1)—C(3)—C(2')	120.9 (2)	N(2)—C(7)—C(6')	120.6 (2)
C(2)—N(1)—C(3)	118.8 (2)	C(6)—N(2)—C(7)	118.1 (2)

compared with the C—C and C—N lengths in TMP at 300 K (1.380, 1.330 Å; Braam, Eshuis & Vos, 1980), in TMP at 100 K (1.406, 1.347 Å; Braam, Eshuis & Vos, 1980) and in pyrazine at 184 K (1.3875, 1.3330 Å; de With, Harkema & Feil, 1976). The agreement is reasonable if account is taken of the decrease in observed bond lengths with increasing temperature due to thermal effects. The C—CH₃ lengths in TMP.3H₂O (average 1.492 Å) show good agreement with the room-temperature values of the water-free compound (1.494 Å). They are shorter, however, than the C—CH₃ bonds in durene at room temperature (1.520 Å; Stam, 1972), presumably because the N atom in the ring exerts a smaller repulsion on CH₃ than a C atom. The ring angles at C, average 120.8°, are larger and the ring angles at N, average value 118.3°, smaller than 120°. For water-free TMP at 100 K the average values are C—C—N = 120.80° and C—N—C = 118.38°; in pyrazine C—C—N = 121.91° is larger and C—N—C = 116.18° smaller than for the TMP molecules. The fact that all three compounds have C—N—C < 120° can be explained by the repulsion between the N atom lone pair of electrons and the C—N bonds. Comparison of the TMP.3H₂O and TMP values shows that the influence of the hydrogen bridges on this repulsion is negligible. Comparison with the pyrazine values reveals a significant effect of the CH₃ groups, evidently due to the strong repulsive interaction of these groups with their neighbours. The strain in the TMP molecule in TMP.3H₂O also results in deviations of the C(methyl) atoms from the plane of the aromatic rings; distances vary from 0.013 to 0.039 Å.

In the crystal the two TMP molecules are not exactly equal and have lower symmetry than expected for free TMP molecules. The mirror plane through N...N and perpendicular to the aromatic plane is lacking, in contrast to water-free TMP where the deviations from this symmetry are not significant. The asymmetry

seems to be induced by the O atoms of the water molecules, which are relatively close to the TMP molecules. For molecule *A* (Fig. 1) O(1) is closer to C(1) and C(2) than to C(3) and C(4), resulting in an extra attraction between O(1) and C(2). For C(1) the environment of O atoms is such that the resulting attractive C...O force is approximately zero. For molecule *B* O(2) is relatively close to C(7); in this case there is no cancelling of C(8)...O attractions, but a net resulting force approximately in the C(8)...O(2) direction. These C...O forces give a tentative explanation for the observed variations in molecular geometry if it is assumed that the molecules do not respond to these forces by rigid-body translations or rotations.

The computations were carried out on a Cyber 74/18 computer at the Computation Center of the University of Groningen.

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1,5-Dithiacyclooctane-3,7-dione Bis(ethylene acetal)

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Abstract. $C_{10}H_{16}O_4S_2$, monoclinic, $P2_1/c$, $a = 5.489(2)$, $b = 10.821(4)$, $c = 10.190(4)$ Å, $\beta = 105.87(3)^\circ$, $Z = 2$, $D_c(140\text{ K}) = 1.51$, $D_x(298\text{ K}) = 1.47$ Mg m⁻³. The structure refined to $R = 0.024$ for 674 reflections with $I > 3\sigma(I)$. A rather long S...S' distance of 3.576(1) Å spans the neutral eight-membered ring.

Introduction. The crystal structure determination of the title compound was undertaken primarily to determine the non-bonded S...S distance across a neutral, dithioether eight-membered ring. Although of interest in its own right, the title compound was chosen because it was easily synthesized (Stein, 1978) and because its melting point of 472 K made it more tractable than 1,5-dithiacyclooctane, which is a liquid at room temperature. Interest in the S...S distance stems from several observations, primarily based on studies of 1,5-dithiacyclooctane. The photoelectron spectrum of this compound shows a splitting of the low-energy peak into a doublet, suggesting that the lone

pairs on the two S atoms interact to give bonding and antibonding combinations (Stein, 1978). In addition, oxidation by NOBF₄ in acetonitrile gives rise to a long-lived cation radical and a dication, both of which contain S—S bonds (Musker & Wolford, 1976). Preliminary studies (Hirschon, 1979) on the title compound indicate that it does not form a radical cation under similar conditions. Nevertheless, a through-space interaction between the two S atoms has been implicated when it bridges two Ru atoms (Stein, 1978) by the observation of an intervalence transition in the visible spectrum of the mixed-valence complex.

