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Tetramethylpyrazine–*endo*-norbornene-*cis*-5,6-dicarboxylic acid (1/2)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.008 Å
R factor = 0.096
wR factor = 0.326
Data-to-parameter ratio = 12.9

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

In the title complex, $2C_9H_{10}O_4\cdot C_8H_{12}N_2$, there is an inversion centre at the centre of the 2,3,5,6-tetramethylpyrazine molecule, which is linked to two *endo*-norbornene-*cis*-5,6-dicarboxylic acid molecules *via* O—H···N hydrogen bonds. In the crystal structure, O—H···O and O—H···N hydrogen bonds propagate a one-dimensional zigzag chain, which is extended into layers when combined with longer C—H···O hydrogen bonds.

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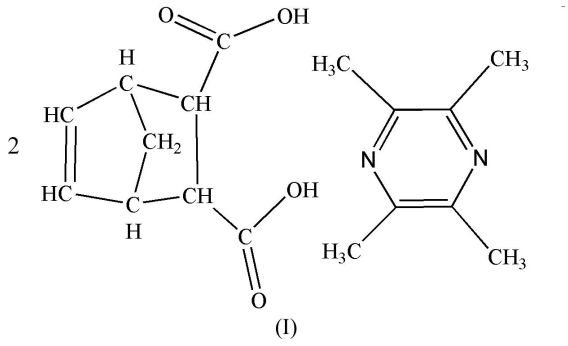
Comment

2,3,5,6-Tetramethylpyrazine (TMP) is one of the most important active ingredients of the traditional Chinese herbal medicine Ligusticum wallichii Franchat (Chung Chong) (Zhang *et al.*, 2003). There are numerous examples of pharmacokinetic studies of the antiplatelet activity of TMP (Sheu *et al.*, 1997; Tsai & Liang, 2001). TMP may act not only as a bridging ligand in metal complexes (Shao *et al.*, 2004), but also as a guest molecule in inclusion compounds (Smyth *et al.*, 1996). We report here the structure of the title adduct, (I).



(I)

One TMP molecule, having an inversion centre at the centre of the pyrazine ring, links two *endo*-norbornene-*cis*-5,6-dicarboxylic acid (END) molecules *via* O3—H3···N3 hydrogen bonds (see Table 2 and Fig. 1). This pattern is reinforced by a C1—H1*C*···O3 weak hydrogen bond. The TMP molecule in

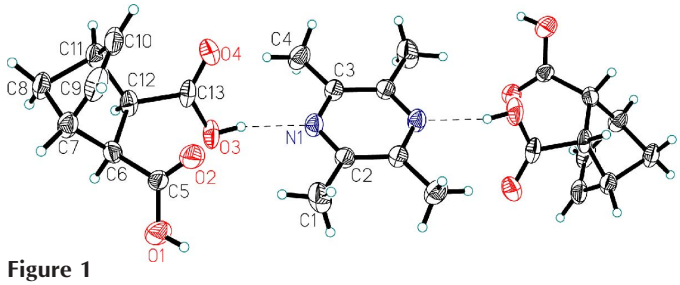


Figure 1
The structure of (I), showing the atom numbering and displacement ellipsoids at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operation $3-x, 2-y, 1-z$

(I) appears to be unprotonated and the C2—N1—C3 angle [119.7 (4)°] is smaller than the corresponding angle in a monoprotonated TMP [124.2 (3)°] (Chen *et al.*, 2005). The C—O bonds in the carboxyl groups, *viz*. O1—C5 = 1.296 (6) Å and O4—C13 = 1.308 (7) Å differ significantly from O2—C5 = 1.215 (6) Å and O3—C13 = 1.201 (7) Å, indicating that the carboxyl groups are unionized. The plane of the pyrazine ring of TMP makes angles of 59.49 (2) and 56.92 (2)°, respectively, with the carboxyl planes C13/O3/O4/H3 and C5/O1/O2/H1.

In the crystal structure, an O1—H1···O2^{i} hydrogen bond forms a one-dimensional zigzag chain along the [$\bar{1}$10] direction (Fig. 2 and Table 2). The hydrogen-bonding pattern, as shown in Fig. 2, could be described in graph-set notation (Etter, 1990; Grell *et al.*, 2000) as $C_2^2(16)R_2^2(8)$. Neighbouring chains are interrelated by translation, and are related by a C8—H8*A*···O4^{ii} weak hydrogen bond to form a layer parallel to (001).

Experimental

endo-Norbornene-*cis*-5,6-dicarboxylic acid (2 mmol, 0.37 g) was added slowly to a solution (20 ml) of 2,3,5,6-tetramethylpyrazine (1 mmol, 0.14 g) in ethanol. The mixture was stirred for several minutes and left to stand at room temperature for about two weeks; colourless block-shaped crystals were obtained.

Crystal data

$C_9H_{10}O_4{\cdot}0.5C_8H_{12}N_2$
M_r = 250.27
Triclinic, $P\bar{1}$
a = 6.106 (2) Å
b = 9.293 (3) Å
c = 11.580 (4) Å
α = 101.875 (8)°
β = 97.890 (6)°
γ = 98.590 (8)°
V = 626.1 (4) Å^3
Z = 2
D_x = 1.327 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 986 reflections
θ = 2.7–24.4°
μ = 0.10 mm^{-1}
T = 298 (2) K
Block, colourless
0.22 × 0.13 × 0.12 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.979, T_{max} = 0.988
3212 measured reflections
2149 independent reflections
1374 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 25.0°
$h = -6 \rightarrow 7$
$k = -11 \rightarrow 9$
$l = -13 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.096
$wR(F^2)$ = 0.326
S = 1.22
2149 reflections
167 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.296 (6)	O3—C13	1.308 (7)
O2—C5	1.215 (6)	O4—C13	1.201 (7)
C2—N1—C3	119.7 (4)	O4—C13—O3	123.2 (5)
O2—C5—O1	122.8 (5)		

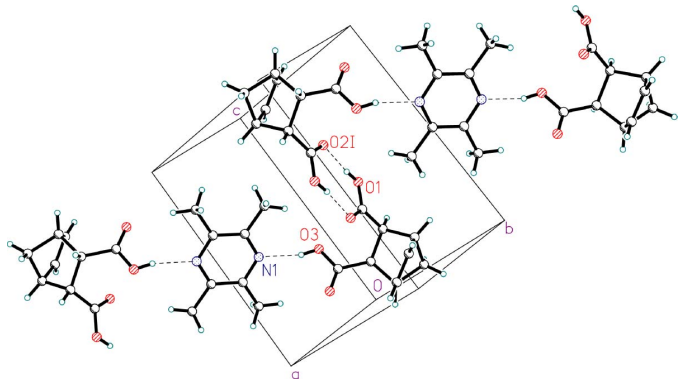


Figure 2
The zigzag chain formed by hydrogen-bonding interactions, which are shown as dashed lines. The suffix I denotes the symmetry code (2 − x, 2 − y, 1 − z).

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.82	1.88	2.696 (5)	174
O3—H3···N1	0.82	1.92	2.715 (5)	164
C1—H1*C*···O3	0.96	2.59	3.399 (5)	142
C8—H8*A*···O4^{ii}	0.97	2.46	3.361 (5)	154

Symmetry codes: (i) 2 − x, 2 − y, 1 − z; (ii) x − 1, y, z.

All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of Csp^2—H = 0.93 Å, with U_{iso} = 1.2U_{eq}(C), Csp^3—H = 0.96 Å, with U_{iso} = 1.5U_{eq}(C), and O—H = 0.82 Å, with U_{iso} = 1.2U_{eq}(O).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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References

Bruker (2002). *SADABS* (Version 2.03), *SAINT* (Version 6.02), *SMART* (Version 5.62) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, D. M., Xia, F. Y., Hu, M. L., Li, L. & Jin, Z. M. (2005). *Acta Cryst.* E**61**, o419–o420.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Grell, J., Bernstein, J. & Tinhofer, G. (2000). *Acta Cryst.* B**56**, 166–179.
Shao, Z.-H., Luo, J., Cai, R.-F., Zhou, X.-G., Weng, L.-H. & Chen, Z.-X. (2004). *Acta Cryst.* C**60**, m250–m253.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. Release 97-2. University of Göttingen, Germany.
Sheu, J. R., Kan, Y. C., Hung, W. C., Ko, W. C. & Yen, M. H. (1997). *Thromb. Res.* **88**, 259–270.
Smyth, M. V., Bailey, R. D. & Pennington, W. T. (1996). *Acta Cryst.* C**52**, 2170–2173.
Tsai, T. H. & Liang, C. C. (2001). *Int. J. Pharm.* **216**, 61–66.
Zhang, Z. H., Wei, T. T., Hou, J. W., Li, G. S., Yu, S. Z. & Xin, W. J. (2003). *Life Sci.* **72**, 2465–2472.