*Acta Cryst.* (1992). C**48**, 2269–2271

# A Tetragonal Form of Tetra(2-pyridyl)pyrazine (TPPZ)

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(*Received* 25 *August* 1992; *accepted* 3 *September* 1992)

## Abstract

The tetragonal form of 2,3,5,6-tetra(2-pyridyl)pyrazine (TPPZ-I) possesses $C_i$ symmetry. The pyridine rings *A* and *B* are inclined toward the pyrazine ring by 59.0(1) and 46.4(1)°, respectively, and toward one another by 60.4(1)°. The shortest intramolecular distance is that between the pyrazine N(1) and the pyridine N(2) atoms [2.907(3) Å], while distance N(3)···C(4*a*) is 3.297(4) Å. Pyridine rings *A* and *A'* have been rotated by more than 180° with respect to the orientation observed in the monoclinic form, TPPZ-II, which also possesses $C_i$ symmetry. Both molecules have planar pyrazine rings.

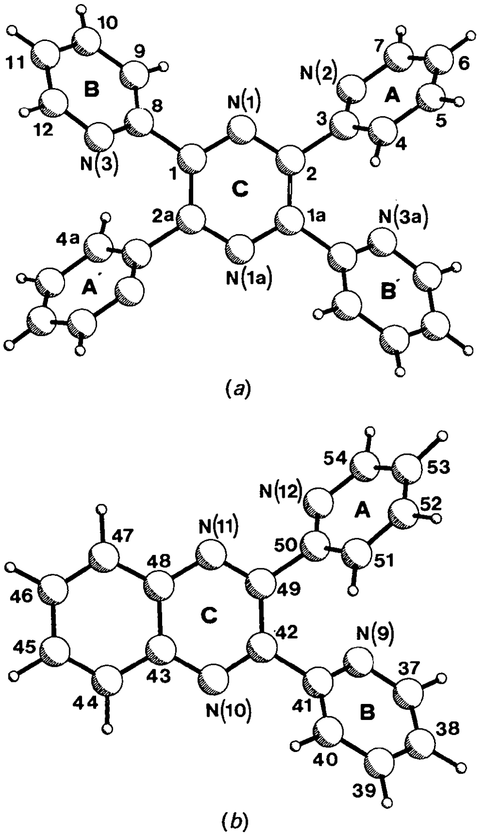

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) plot of (*a*) the tetragonal form of TPPZ-I and (*b*) BPQ-I.

## Comment

The ligand tetra(2-pyridyl)pyrazine [TPPZ, (1)] was first synthesized by Goodwin & Lions (1959). While preparing transition-metal complexes of TPPZ (Graf, Greaves & Stoeckli-Evans, 1992) it was found that with a metal-to-ligand ratio of only 1:1 in the reaction of TPPZ with

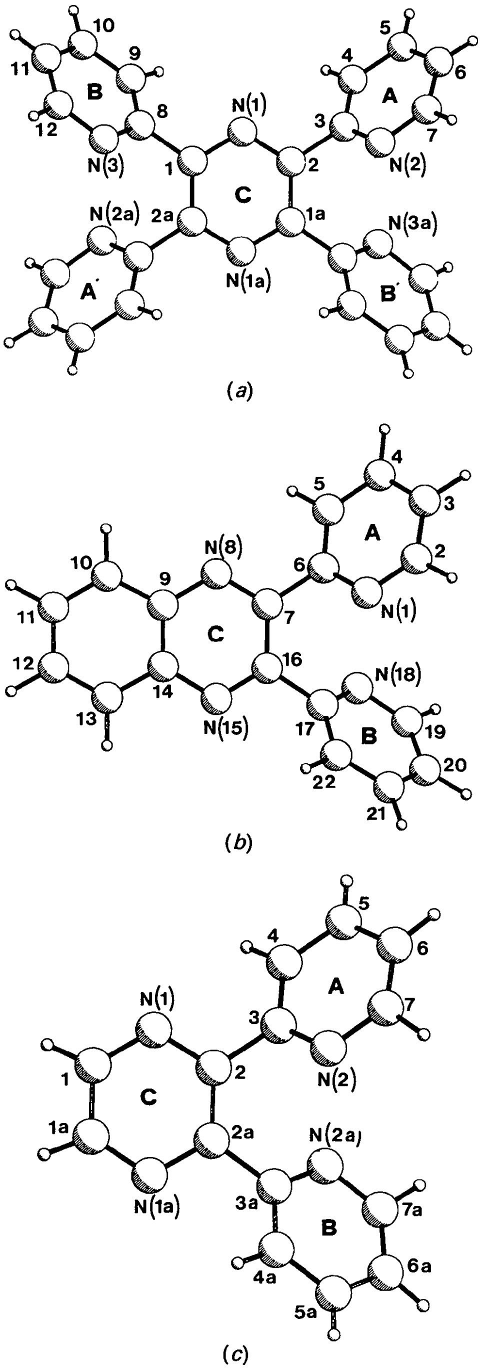

Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) plot of (*a*) the monoclinic form of TPPZ-II, (*b*) BPQ-II and (*c*) BPPZ.

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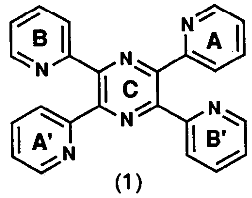
$ZnCl_2$ in water no complex was formed but slow evaporation of the solution gave crystals of monoclinic TPPZ-II. Ethanol was then added and the solution kept at 323 K for 4 h. On cooling a small quantity of a mononuclear five-coordinate $Zn^{II}$ complex was formed (Graf *et al.*, 1992) and a large number of transparent block-like crystals. The structure analysis of the latter showed them to be a new tetragonal form of the title compound, TPPZ-I (Fig. 1*a*). The final atomic coordinates and thermal parameters of this compound are given in Table 1. Interatomic bond distances and angles are given in Table 2. The structure of the monoclinic form TPPZ-II, recrystallized from $CHCl_3$, was recently published (Bock, Vaupel, Näther, Ruppert & Havlas, 1992) (Fig. 2*a*). We have also solved the structure of the monoclinic form recrystallized from $CH_2Cl_2$, with identical results. In TPPZ-II the pyridine N atoms are 3.237(3) Å apart. The pyridine rings *A* and *B* are inclined toward the pyrazine ring *C* by 48.9(1) and 51.7(1)°, respectively, and to one another by 62.4(1)°. A similar compound 2,3-bis(2-pyridyl)quinoxaline (BPQ) has also been observed in two forms (Figs. 1*b* and 2*b*). In BPQ-I (Goodwin, Pennington & Petersen, 1990) the pyrazine ring is almost planar (twist angle 0.035°). In BPQ-II (Rasmussen, Richter, Yi, Place & Brewer, 1990) the pyrazine ring is twisted by 5.7°. The twisting of the pyrazine ring has also been observed in zinc and copper complexes of TPPZ (Graf *et al.*, 1992), and rhodium (Rasmussen *et al.*, 1990), ruthenium (Rillema, Taghdiri, Jones, Keller, Wrol, Meyer & Levy, 1987) and copper (Goodwin *et al.*, 1990) complexes of BPQ. The orientation of the two pyridine rings in 2,3-bis(2-pyridyl)pyrazine (BPPZ, Fig. 2*c*) (Huang, Pennington & Petersen, 1991) is also similar to that in TPPZ-II and BPQ-II. In Table 3 we compare similar dihedral angles between the pyridine rings *A* and *B* and the pyrazine ring *C* in the five compounds and similar intramolecular distances. It can be seen that the geometry in TPPZ-I and that in BPQ-I are very similar, more so than in TPPZ-II, BPQ-II and BPPZ. The largest differences concern the shortest intramolecular contacts. For example, the distance N(3)···C(4*a*) is 3.297 Å in TPPZ-I compared to 3.180 Å for the distance N(9)···C(51) in BPQ-I. The same tendency is observed in TPPZ-II, BPQ-II and BPPZ. For example, the distance N(2)···N(3*a*) is 3.237 Å in TPPZ-II, significantly larger than the distance N(1)···N(18) of 3.017 Å in BPQ-II or the distance N(2)···N(2*a*) of 2.962 Å in BPPZ. This difference is also reflected in the dihedral angle of 31.69° between rings *A* and *C* in BPQ-II, which is much smaller than that in TPPZ-II (48.9°) or in BPPZ (42.2°).



(1)

## Experimental

### Crystal data

$C_{24}H_{16}N_6$
$M_r = 388.43$
Tetragonal
$I4_1/a$
$a = 17.121$ (1) Å
$c = 13.241$ (1) Å
$V = 3881.3$ (4) Å$^3$
$Z = 8$
$D_x = 1.329$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 13 reflections
$\theta = 14.00\text{-}19.00°$
$\mu = 0.08$ mm$^{-1}$
$T = 293$ K
Large block with many faces
0.34 × 0.30 × 0.30 mm
Transparent

### Data collection

Stoe AED-2 four-circle diffractometer
$\omega/\theta$ scans
Absorption correction: none
2217 measured reflections
2217 independent reflections
1205 observed reflections [$I_{\rm net} > 2.5\sigma(I_{\rm net})$]
$R_{\rm int} = 0.000$ (one equivalent only)
$\theta_{\rm max} = 27.45°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 17$
4 standard reflections
frequency: 60 min
intensity variation: 1.0%

### Refinement

Refinement on $F$
Final $R = 0.053$
$wR = 0.072$
$S = 1.07$
1205 reflections
168 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F)+0.0040F^2]$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.25$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.39$ e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| N(1) | 0.69608 (13) | 0.30985 (11) | 0.75865 (15) | 0.0292 (10) |
| N(2) | 0.69491 (13) | 0.37021 (13) | 0.96385 (17) | 0.0355 (11) |
| N(3) | 0.66755 (14) | 0.29008 (13) | 0.50169 (16) | 0.0373 (12) |
| C(1) | 0.72462 (14) | 0.28903 (14) | 0.66872 (18) | 0.0267 (11) |
| C(2) | 0.72058 (14) | 0.27115 (14) | 0.84028 (18) | 0.0263 (12) |
| C(3) | 0.68468 (15) | 0.29508 (15) | 0.93833 (18) | 0.0282 (11) |
| C(4) | 0.64266 (18) | 0.24254 (19) | 0.99581 (23) | 0.0426 (15) |
| C(5) | 0.60849 (20) | 0.26871 (22) | 1.0838 (3) | 0.0517 (18) |
| C(6) | 0.61887 (19) | 0.34546 (21) | 1.11180 (23) | 0.0499 (17) |
| C(7) | 0.66233 (17) | 0.39385 (18) | 1.05020 (22) | 0.0409 (14) |
| C(8) | 0.69147 (15) | 0.33290 (15) | 0.58050 (18) | 0.0289 (12) |
| C(9) | 0.68398 (20) | 0.41349 (17) | 0.58501 (22) | 0.0439 (16) |
| C(10) | 0.64952 (22) | 0.45126 (20) | 0.50484 (24) | 0.0519 (18) |
| C(11) | 0.62257 (20) | 0.40835 (18) | 0.42401 (23) | 0.0455 (16) |
| C(12) | 0.63363 (19) | 0.32896 (18) | 0.42563 (22) | 0.0449 (17) |

Table 2. *Geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| N(1)—C(1) | 1.336 (3) | C(2)—C(3) | 1.494 (3) |
| N(1)—C(2) | 1.335 (3) | C(3)—C(4) | 1.380 (4) |
| N(2)—C(3) | 1.341 (3) | C(4)—C(5) | 1.378 (5) |
| N(2)—C(7) | 1.335 (4) | C(5)—C(6) | 1.377 (5) |
| N(3)—C(8) | 1.339 (3) | C(6)—C(7) | 1.380 (5) |
| N(3)—C(12) | 1.340 (4) | C(8)—C(9) | 1.387 (4) |
| C(1)—C(2*a*) | 1.399 (3) | C(9)—C(10) | 1.376 (4) |
| C(1)—C(8) | 1.500 (3) | C(10)—C(11) | 1.378 (5) |
| C(2)—C(1*a*) | 1.399 (3) | C(11)—C(12) | 1.373 (4) |

| | | | |
|---|---|---|---|
| C(1)—N(1)—C(2) | 118.31 (21) | C(3)—C(4)—C(5) | 118.4 (3) |
| C(3)—N(2)—C(7) | 116.87 (25) | C(4)—C(5)—C(6) | 118.9 (3) |
| C(8)—N(3)—C(12) | 116.50 (24) | C(5)—C(6)—C(7) | 118.9 (3) |
| N(1)—C(1)—C(2*a*) | 121.20 (21) | N(2)—C(7)—C(6) | 123.3 (3) |
| N(1)—C(1)—C(8) | 114.97 (21) | N(3)—C(8)—C(1) | 116.63 (22) |
| C(2*a*)—C(1)—C(8) | 123.80 (22) | N(3)—C(8)—C(9) | 123.35 (24) |
| N(1)—C(2)—C(1*a*) | 120.49 (22) | C(1)—C(8)—C(9) | 119.97 (23) |
| N(1)—C(2)—C(3) | 115.99 (21) | C(8)—C(9)—C(10) | 118.3 (3) |
| C(1*a*)—C(2)—C(3) | 123.51 (21) | C(9)—C(10)—C(11) | 119.5 (3) |
| N(2)—C(3)—C(2) | 115.35 (22) | C(10)—C(11)—C(12) | 118.0 (3) |
| N(2)—C(3)—C(4) | 123.64 (25) | N(3)—C(12)—C(11) | 124.3 (3) |
| C(2)—C(3)—C(4) | 121.00 (24) | | |

Table 3. *A comparison of various dihedral angles* (°) *and short intramolecular distances* (Å) *in* TPPZ-I *and* BPQ-I, *and* TPPZ-II, BPQ-II *and* BPPZ

| | TPPZ-I | BPQ-I | TPPZ-II | BPQ-II | BPPZ |
|---|---|---|---|---|---|
| Angles | | | | | |
| ∠*AB* | 60.4 | 58.9 | 62.4 | 60.6 | 54.1 |
| ∠*AC* | 59.0 | 54.0 | 48.9 | 31.7 | 42.2 |
| ∠*BC* | 46.4 | 45.2 | 51.7 | 46.4 | 42.2 |
| Distances | | | | | |
| N(1)···N(2) | 2.907 | 2.803 | | | |
| N(1)···C(9) | 2.912 | 2.910 | | | |
| N(3)···C(4$a^{i}$) | 3.297 | 3.180 | | | |
| N(1)···C(4) | | | 2.939 | 2.854 | 2.859 |
| N(1)···C(9) | | | 2.958 | 2.941 | 2.859 |
| N(2)···N(3$a^{ii}$) | | | 3.237 | 3.017 | 2.962 |

Symmetry operations: (i) $1.5 - x, 0.5 - y, 1.5 - z$; (ii) $2 - x, -y, -z$.

The sample of TPPZ used in the synthesis of the zinc(II) complex was originally synthesized according to Goodwin & Lions (1959) and recrystallized from $CH_2Cl_2$. The structure was solved by direct methods using the *NRCVAX* system (Gabe, Le Page, Charland, Lee & White, 1989) which was used for all further calculations. The H atoms were located from difference maps.

We wish to thank the Swiss National Science Foundation for financial support.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55512 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1025]

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*Acta Cryst.* (1992). C**48**, 2271-2273

# Structure of Eltoprazine

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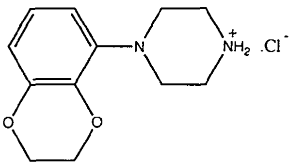
(*Received* 3 *March* 1992; *accepted* 18 *August* 1992)

## Abstract

The piperazine ring of 1-(2,3-dihydro-1,4-benzodioxin-5-yl)piperazine hydrochloride is oriented in such a way that the C atoms of one of the C—C bonds are almost coplanar with the plane of the phenyl ring. The piperazine ring adopts an almost perfect chair conformation and the dihydro-1,4-dioxine ring a half-chair conformation. The protonated secondary amino group donates two strong hydrogen bonds to symmetry-related $Cl^-$ anions.

## Comment

The psychoactive drug eltoprazine (1) reduces aggressive behaviour (Mos & Olivier, 1988; Olivier, Mos, van der Heyden & Hartog, 1989) and enhances social interest and exploration in rats (Olivier, Mos, van der Heyden & Hartog, 1989). This compound has recently been shown to bind at serotonergic (5-$HT_1$) receptor sites in the rat brain (Sijbesma, Schipper & de Kloet, 1990) and its conformation might therefore be very useful in developing pharmacophores for serotonergic receptors.



(1)

The X-ray results show that the C6—C5—N1—C9 torsional angle, the main source of conformational freedom, is 11(1)°. This means that one of the C—C bonds of the piperazine ring is almost coplanar with the plane of the phenyl ring. The piperazine ring appears to be in an almost perfect chair conformation and the dihydro-1,4-dioxine ring adopts a half-chair conformation. The terminal secondary amino group is protonated and donates two strong hydrogen bonds to $Cl^-$ at $x, 1+y, z$ and $Cl^-$ at $2-x, \frac{1}{2}+y, \frac{1}{2}-z$ with geometries N···$Cl^-$, N—H, H···$Cl^-$ and N—H···$Cl^-$ of 3.172(8), 1.08(1), 2.125(8) Å and 162.7(8)° and 3.045(8), 1.08(1), 1.980(8) Å and 168.3(8)° respectively.

0108-2701/92/122271-03$06.00