

3,6-Di-2-pyridyl-4-[(2-pyridyl)carbonyldiazenyl]- (2-pyridyl)methyl]-1*H*-1,2,4,5-tetrazine: the proton- assisted hydrolysis product of 3,6-di-2-pyridyl-1,2,4,5- tetrazine (dptz)

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$

R factor = 0.056

wR factor = 0.086

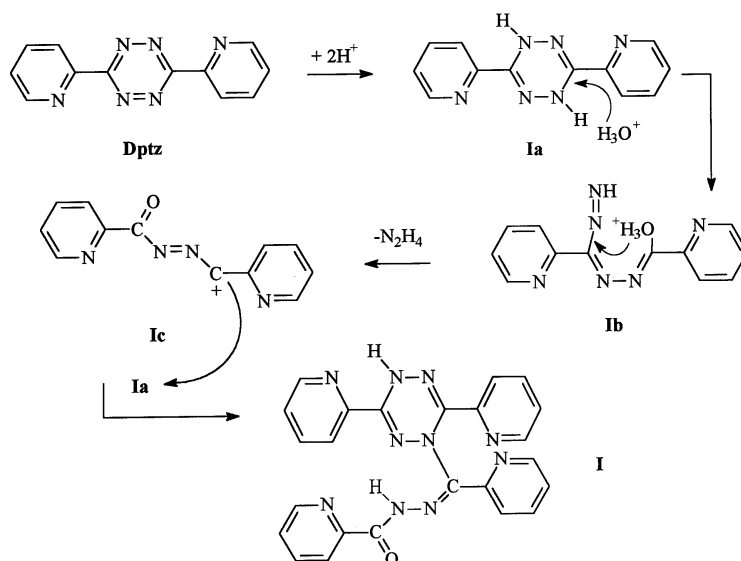
Data-to-parameter ratio = 11.6

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

In the title compound, $\text{C}_{24}\text{H}_{18}\text{N}_{10}\text{O}$, the tetrazine ring adopts a boat conformation. The structure is stabilized by strong intramolecular and weak intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds.

Comment

3,6-Di-2-pyridyl-1,2,4,5-tetrazine (dptz), a well known functional molecule, has been extensively investigated as a coordinative π -acceptor moiety of transition-metal complexes (Ernst *et al.*, 1988; Klein *et al.*, 1998; Schwach *et al.*, 1999; Glockle *et al.*, 1999) and as a building block for supramolecular assemblies based on its role in bridging two metal centers (Campos-Fernandez *et al.*, 1999; Bu *et al.*, 2000). This type of aromatic compound also exhibits proton-sponge properties (Stabb *et al.*, 1988; Robertson *et al.*, 1998), and can act as an external proton acceptor through formation of $\text{N}-\text{H}\cdots\text{Y}$ hydrogen bonds. A recent study investigated the crystal structure of the diprotonated perchlorate salt of dptz, 3,6-di-2-pyridinio-1,2,4,5-tetrazine diperchlorate, forming a chain structure through $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding (Liu *et al.*, 2001). However, during the course of our study on the HAc protonated salt of dptz an unexpected hydrolysis reaction was observed, which is proton-assisted. In this report, we describe the crystal structure of a new compound, 3,6-di-2-pyridyl-4-[(2-pyridyl)carbonyldiazenyl](2-pyridyl)methyl]-1*H*-1,2,4,5-tetrazine, (I), and the possible mechanism of hydrolysis (see Scheme below).



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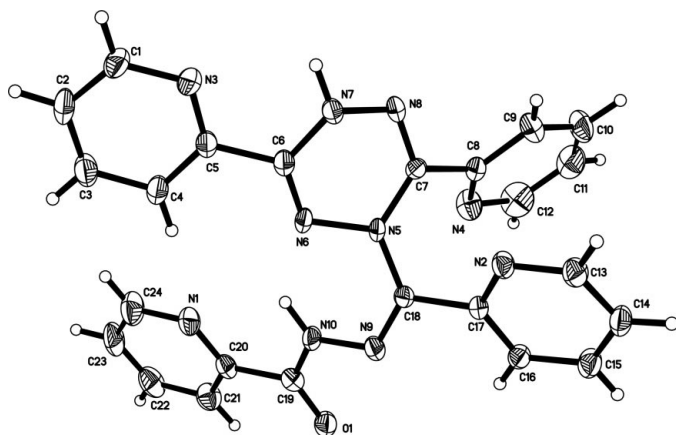


Figure 1
ORTEP (Johnson, 1976) view of the title compound shown with 30% probability ellipsoids.

The possible hydrolysis mechanism is postulated in the Scheme above. Dptz is easily protonated in acid solution and becomes extremely susceptible to nucleophilic attack by water (1a). The tetrazine ring is cleaved and a water molecule is added to form an enolic structure (1b), and it is easily converted to a carbonyl group. After losing hydrazine, the residual cations attack (1a) and produce the new compound (I).

A perspective view of the neutral molecule (I) including the atomic numbering scheme is shown in Fig. 1. The six-membered ring C6/N6/N5/C7/N8/N7 loses the aromaticity of the original tetrazine ring, and adopts a boat conformation, with N7 and N5 deviating by 0.388 (3) and 0.373 (2) Å, respectively, from the basal N8/C6/N6/C7 plane. The C6–N6 and C7–N8 bond distances are 1.265 (4) and 1.274 (4) Å, typical of C=N double bonds. The other C–N bonds (C6–N7 and N5–C7) and the two N–N bonds have single-bond character. The pyridine rings A (C1–C5/N3), B (C8–C12/N4), C (C20–C24/N1) and D (C13–C17/N2) are essentially planar. Plane A forms dihedral angles of 37.6 (2), 25.9 (2) and 20.9 (2)° with planes B, C and D, respectively. Plane B forms dihedral angles of 49.1 (2) and 45.7 (2)° with planes C and D, respectively, and the dihedral angle between planes C and D is 5.0 (2)°. The C19–O1 bond length is 1.237 (4) Å, indicating a carbonyl group.

The structure is stabilized by a strong intramolecular N10–H10···N6 hydrogen bond with an N···N separation of 2.683 (5) Å and an N–H···N angle of 127 (2)°. Furthermore, there exists a weak intermolecular N7–H7···N9ⁱ [symmetry code: (i) $x + 1, y, z$] interaction with an N···N separation of 3.282 (5) Å and an N–H···N angle of 146 (2)°, which links the molecules to form a linear chain structure.

Experimental

Orange single crystals of the title compound suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether

into an acetonitrile solution of dptz in the presence of HAC, in 45% yield. Analysis found: C 62.17, H 3.93, N 30.12%; calculated for C₂₄H₁₈N₁₀O: C 62.32, H 3.82, N 30.29%. IR (KBr, cm⁻¹): 3425 (m), 1682 (vs), 1588 (m), 1503 (s), 1464 (s), 1433 (vs), 1415 (s), 1014 (s), 791 (s), 745 (m).

Crystal data

C₂₄H₁₈N₁₀O
M_r = 462.48
Triclinic, P1
a = 7.949 (5) Å
b = 11.540 (7) Å
c = 12.118 (7) Å
α = 83.200 (11)°
β = 85.971 (12)°
γ = 77.557 (11)°
V = 1076.8 (11) Å³

Z = 2
D_x = 1.426 Mg m⁻³
Mo Kα radiation
Cell parameters from 4426 reflections
θ = 2.4–25.0°
μ = 0.10 mm⁻¹
T = 293 (2) K
Prism, orange
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)
T_{min} = 0.972, T_{max} = 0.981
4478 measured reflections

3752 independent reflections
2474 reflections with I > 2σ(I)
R_{int} = 0.052
θ_{max} = 25.0°
h = -8 → 9
k = -13 → 13
l = -7 → 14

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.056
wR(F²) = 0.086
S = 0.88
3752 reflections
324 parameters

H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(F_o²) + (0.005P)²]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.008
Δρ_{max} = 0.17 e Å⁻³
Δρ_{min} = -0.17 e Å⁻³

Table 1

Selected interatomic distances (Å).

O1–C19	1.232 (4)	N7–N8	1.423 (4)
N5–C7	1.416 (4)	N8–C7	1.274 (4)
N5–N6	1.422 (3)	N9–C18	1.285 (4)
N6–C6	1.265 (4)	N9–N10	1.389 (3)
N7–C6	1.401 (4)	N10–C19	1.355 (4)

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXL97.

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