

Crystal structures of products from the BBr_3 -promoted demethylation of 3-(methoxymethyl)-6-phenyl-1,2,4,5-tetrazine

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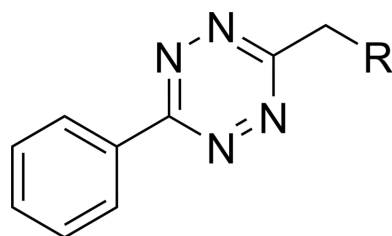
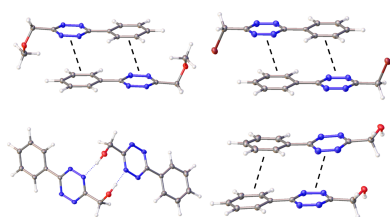
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Keywords: 1,2,4,5-tetrazine; hydrogen bonds; crystal structure; synthesis.**CCDC references:** 2587346; 2587345; 2587344**Supporting information:** this article has supporting information at journals.iucr.org/e

The BBr_3 -promoted demethylation of 3-(methoxymethyl)-6-phenyl-1,2,4,5-tetrazine, $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}$, resulted in the alcohol (6-phenyl-1,2,4,5-tetrazin-3-yl)-methanol, $\text{C}_9\text{H}_8\text{N}_4\text{O}$, and the bromide 3-(bromomethyl)-6-phenyl-1,2,4,5-tetrazine, $\text{C}_9\text{H}_7\text{BrN}_4$. All three compounds were analysed by nuclear magnetic resonance (NMR) spectroscopy in solution and by single-crystal X-ray diffraction using non-spherical scattering factors for structure refinement. The substrate as well as the corresponding bromide form π - π interactions between antiparallel stacks of molecules. In contrast, due to the intermolecular hydrogen bonds present, which lead to the formation of a bent dimer, the alcohol forms only very weak parallel π - π stacks. Corresponding $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds are established between the hydroxy group and an N atom of a neighbouring tetrazine molecule, an only rarely explored structural feature of 1,2,4,5-tetrazines.

1. Chemical context

1,2,4,5-Tetrazines, first described by Pinner (1893), are electron-deficient heterocycles of particular relevance in fast and chemoselective cycloaddition reactions (Zhao *et al.*, 2022). While structurally simple 1,2,4,5-tetrazines (herein further abbreviated as tetrazines) are well-known in the literature, for many modern applications, tetrazines substituted at the 3- and 6-positions are needed (Yim *et al.*, 2026). In particular, tetrazines modified with a hydroxymethyl group at the 3-position and derivatives thereof are frequently used as marker molecules in biochemical applications (Baalmann *et al.*, 2019; Tu *et al.*, 2020; Wang *et al.*, 2022). Early reports on the synthesis and derivatization of such tetrazines were provided by Lang *et al.* (1975) through the synthesis of a panel of 3,6-disubstituted tetrazines. Out of this library, 3-(methoxymethyl)-6-phenyl-1,2,4,5-tetrazine (**1**) was synthesized (Tu *et al.*, 2019), and the BBr_3 -promoted demethylation re-investigated to obtain the deprotected alcohol (**2**) and the bromide (**3**) as a side product (Fig. 1). In the scope of the present investigations, tetrazines (**1**)–(**3**) were characterised by NMR spectroscopy in solution and by single-crystal X-ray diffraction.

R = OMe **1**R = OH **2**R = Br **3**

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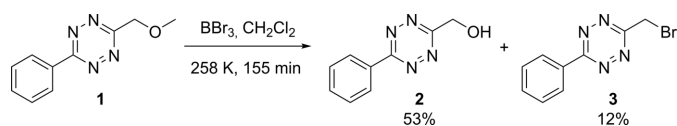


Figure 1

Treatment of tetrazine (**1**) with BBr_3 afforded both alcohol (**2**) and bromide (**3**).

2. Structural commentary

While the structures of tetrazine (**1**) and alcohol (**2**) were clearly confirmed by NMR spectroscopy in solution with ^{13}C $\{^1\text{H}\}$ NMR shifts of the methylene groups at 72.3 and 63.0 ppm, respectively, the strong upfield shift of the bromomethyl group of bromide (**3**) to 27.8 ppm hints to the introduction of a strongly deshielding substituent. However, unambiguous structural proof was given by the results of single-crystal X-ray diffraction.

Both the substrate (**1**) and the bromide (**3**) crystallize in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit each (Fig. 2). In contrast, alcohol (**2**) crystallizes in the monoclinic space group $P2_1/n$ with a hydrogen-bonded dimer in the asymmetric unit (Fig. 3). The two crystallographically independent molecules (**2A/2B**) show close conformational similarity with a root-mean-square deviation of 0.169 Å (Fig. 3, right). The phenyl units of all tetrazines (**1**)–(**3**) show similar bond lengths for all C–C bonds [1.391 (2)–1.401 (2) Å] and all C–N and N–N bonds of the tetrazine

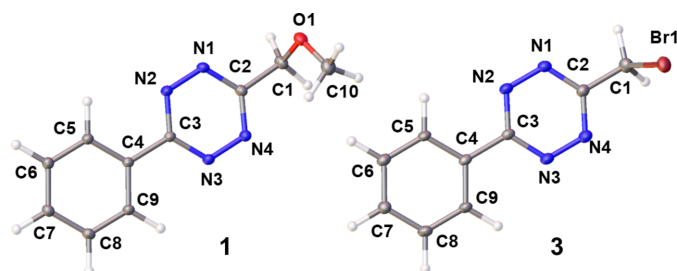


Figure 2

Molecular structures of tetrazine (**1**) and bromide (**3**) with displacement ellipsoids represented at the 50% probability level and H atoms as spheres of arbitrary radius.

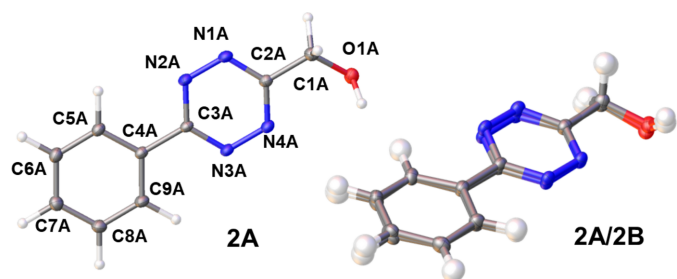


Figure 3

(Left) Molecular structure of alcohol (**2**) with displacement ellipsoids represented at the 50% probability level and H atoms as spheres of arbitrary radius; for the sake of clarity only molecule **A** is shown. (Right) Overlay-plot (generated using the 'match' option within *OLEX2*) of molecules (**2A/2B**) showing their close conformational similarity.

Table 1

Hydrogen-bond geometry (Å, °) for (**2**).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1A}-\text{H1A}\cdots\text{N1B}$	0.969 (12)	1.963 (13)	2.9019 (9)	162.7 (10)
$\text{O1B}-\text{H1B}\cdots\text{N4A}$	0.972 (13)	1.871 (13)	2.8287 (9)	168.2 (11)

units [1.308 (1)–1.353 (1) Å], indicative of their aromaticity with an extended co-planar arrangement of the biaryl moieties. The dihedral angles between the phenyl and tetrazine rings are 3.63 (4)° (**1**), 2.29 (4)° (**2A**), 8.47 (5)° (**2B**), and 2.72 (1)° (**3**). All bond angles agree with values obtained from structurally similar disubstituted tetrazines containing a phenyl and substituted methyl substituents (for details see Section 4). The methoxymethyl group of tetrazine (**1**) and the bromomethyl group of bromide (**3**) accommodate the largest atoms (O and Br), resulting in the smallest torsion angles with 73.17 (8)° for the $\text{N1}-\text{C2}-\text{C1}-\text{O1}$ connection and -74.63 (17)° for the $\text{N4}-\text{C2}-\text{C1}-\text{Br1}$ connection, likely due to repulsion with the N-centered lone pairs of the tetrazine units. Interestingly, the $\text{N1}-\text{C2}-\text{C1}-\text{O1}$ torsion angles of alcohol (**2**) are different from those of (**1**) and (**3**) with -162.92 (7)° for (**2A**) and 16.06 (9)° for (**2B**), an observation that may be explained by the intermolecular hydrogen-bonding interactions between hydroxy groups and tetrazine-N atoms (see Section 3).

3. Supramolecular features

All of the tetrazines investigated here show $\pi-\pi$ interactions, the strongest between antiparallel stacked molecules of tetrazine (**1**) and bromide (**3**) with centroid-to-centroid

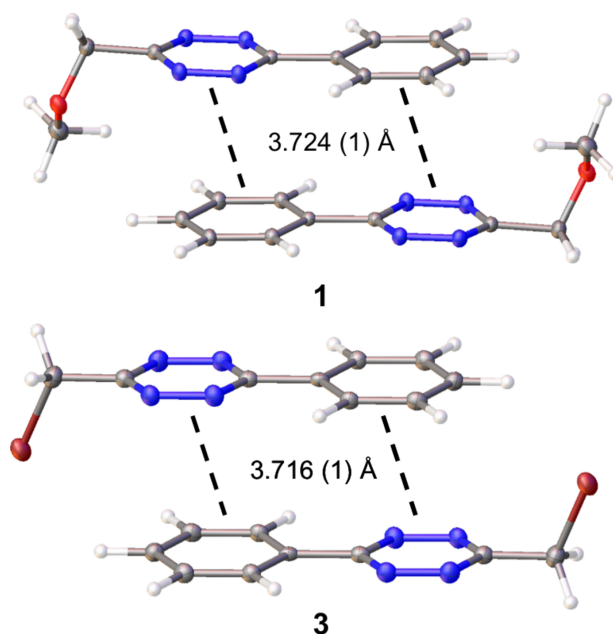


Figure 4

Supramolecular $\pi-\pi$ interactions of molecules of tetrazine (**1**) (top) and bromide (**3**) (bottom) with centroid-to-centroid distances indicated. Displacement ellipsoids are represented at the 50% probability level; symmetry code to obtain the second molecule: (1 $-x$, 1 $-y$, 1 $-z$).

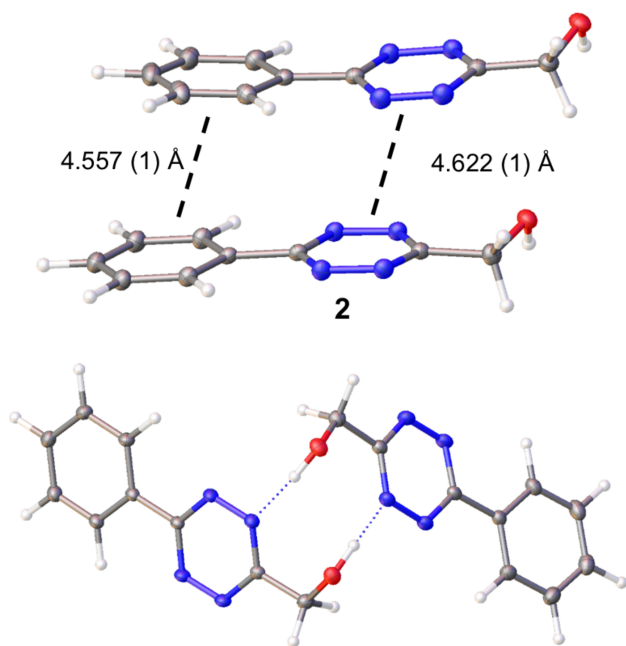


Figure 5

(Top) Supramolecular π - π interactions of molecules of alcohol (**2**) with the centroid-to-centroid distances indicated; (bottom) formation of a dimer through hydrogen bonds (dashed lines). Displacement ellipsoids are represented at the 50% probability level; symmetry code to obtain the second molecule: $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$.

distances of 3.724 (1) Å [slippage of 1.676 (1) Å] between the phenyl/tetrazine rings for (**1**) and of 3.716 (1) Å [slippage of 1.643 (3) Å] for (**3**), respectively (Fig. 4).

Two hydrogen bonds between hydroxy groups and tetrazine N atoms of molecules (**2A**) and (**2B**) form a bent dimer of alcohol (**2**), as shown in Fig. 5, bottom. The drastic reduction in the N1—C2—C1—O1 torsion angle compared with tetrazine (**1**) may be explained by the reduced electron density at the neighbouring N atom, which is attributable to its role as a hydrogen-bond acceptor (Table 1). Similar hydrogen-bonding interactions were described previously for hydroxymethyl substituted tetrazines (Voss *et al.*, 2025).

Interestingly, the intermolecular hydrogen bonds of alcohol (**2**) cause the formation of weakly interacting parallel stacks of molecules without contacts between phenyl/tetrazine ring centroids but with comparably elongated phenyl/phenyl and tetrazine/tetrazine centroid-to-centroid distances of 4.557 (1) Å [slippage of 3.245 (1) Å] and 4.622 (1) Å [slippage of 3.311 (1) Å], respectively (Fig. 5, top). The observation of stronger interactions between antiparallel stacks of tetrazine (**1**) and the bromide (**3**) as compared to parallel stacks of alcohol (**2**) might be favoured by the increased dipole moment between phenyl and tetrazine rings in antiparallel stacks (Huber *et al.*, 2014; Voss *et al.*, 2025).

4. Database survey

A search of the Cambridge Structural Database (CSD version 6.01, November 2025; Groom *et al.*, 2016) using ConQuest

(version 2026.1.0) revealed eight reports for 3-aryl-6-alkyl-1,2,4,5-tetrazines, including CSD refcodes VEMZUM (Voss *et al.*, 2025), CICPOU (Hu & Xu, 2008) and REWDUT (Xu & Hu, 2007). Out of these, the lengths of all aromatic C—C, C—N and N—N bonds are identical within a 3σ margin of error. With dihedral angles between the phenyl and tetrazine rings of tetrazines (**1**)–(**3**) in the range 2.29 (4) to 8.47 (5)°, similar values between the two rings are also reported for these structurally similar tetrazines.

5. Synthesis and crystallisation

5.1. Materials and methods

Solvents and starting materials were used without further purification, unless noted otherwise. Dichloromethane for reactions was dried by distillation over CaH_2 . The solvents used for extraction and chromatography were of technical grade and were distilled prior to use. Column chromatography was performed with silica gel 60 M (Acros, 0.04–0.063 mm). Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (Merck, F254) using UV light (254 nm) for visualization. 3-(Methoxymethyl)-6-phenyl-1,2,4,5-tetrazine (**1**) was used as starting material and synthesised following a literature protocol (Tu *et al.*, 2019).

5.2. Analytical devices

Nuclear magnetic resonance spectra were recorded on an Avance 500 spectrometer (Bruker) at 298 K using the residual protonated solvent signal [$\delta(^1\text{H})$ of CHCl_3] = 7.26 ppm, $\delta(^{13}\text{C})$ of CDCl_3] = 77.36 ppm] (Fulmer *et al.*, 2010) as internal standard. Electrospray ionisation (ESI) mass spectra (MS) were acquired with an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik) equipped with a nano-ESI source.

5.3. Demethylation of 3-(methoxymethyl)-6-phenyl-1,2,4,5-tetrazine (**1**)

This reaction was performed under an argon atmosphere. Tetrazine (**1**) (593 mg, 2.93 mmol) was dissolved in dry CH_2Cl_2 (8 ml) and the resulting pink solution cooled to 258 K. A solution of BBr_3 (0.70 ml, 7.38 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise to this solution over the course of 10 min while maintaining the temperature. The resulting orange solution was stirred at 258 K for 105 min after which a small part of the solution (50 μl) was withdrawn, added to H_2O (0.3 ml), and the organic layer analysed by TLC (CH_2Cl_2), which indicated full consumption of tetrazine (**1**). After a total of 155 min, the reaction mixture was poured onto ice (50 g) and CH_2Cl_2 (100 ml) was added consecutively. After the ice had melted, the layers were separated and the aqueous layer extracted with CH_2Cl_2 (1 $\times$ 80 ml). The combined pink organic layers were washed with brine (40 ml), dried over MgSO_4 , filtered and evaporated to obtain a pink solid (481 mg). Purification by column chromatography (diameter = 4.5 cm, length = 23 cm) using $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (95:5, v/v) to firstly obtain bromide (**3**) (90.0 mg, 358 μmol , 12%) as a pink solid. Secondly, tetrazine (**1**) (42.3 mg, 209 μmol , 7%) was re-

Table 2
Experimental details.

	(1)	(2)	(3)
Crystal data			
Chemical formula	C ₁₀ H ₁₀ N ₄ O	C ₉ H ₈ N ₄ O	C ₉ H ₇ BrN ₄
<i>M_r</i>	202.22	188.19	251.09
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.3147 (4), 7.4164 (8), 12.2277 (8)	11.8719 (3), 8.4682 (2), 17.2987 (5)	5.2376 (4), 7.5069 (6), 12.0638 (8)
α , β , γ (°)	86.710 (7), 79.913 (6), 78.920 (8)	90, 92.709 (2), 90	89.632 (6), 80.517 (6), 79.451 (7)
<i>V</i> (Å ³)	465.53 (7)	1737.16 (8)	459.80 (6)
<i>Z</i>	2	8	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.10	0.10	4.44
Crystal size (mm)	0.52 × 0.24 × 0.18	0.35 × 0.09 × 0.06	0.35 × 0.29 × 0.09
Data collection			
Diffractometer	SuperNova, Single source at offset/ far, Eos	SuperNova, Single source at offset/ far, Eos	SuperNova, Single source at offset/ far, Eos
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2025)	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2025)	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2025)
<i>T</i> _{min} , <i>T</i> _{max}	0.571, 1.000	0.744, 1.000	0.394, 1.000
No. of measured, independent and observed [<i>I</i> ≥ 2σ(<i>I</i>)] reflections	8849, 3058, 2256	32315, 4666, 3774	7431, 2531, 2136
<i>R</i> _{int}	0.035	0.045	0.048
Refinement			
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.038, 0.061, 1.09	0.030, 0.066, 1.07	0.033, 0.061, 1.03
No. of reflections	3058	4666	2531
No. of parameters	166	317	148
H-atom treatment	H-atom parameters constrained	All H-atom parameters refined	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.34, -0.33	0.21, -0.21	0.81, -0.70

Computer programs: *CrysAlis PRO* (Rigaku OD, 2025), *SHELXT* (Sheldrick, 2015), *OLEX2.refine* (Bourhis *et al.*, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

isolated as a pink solid. Note that since analysis by TLC indicated complete consumption of tetrazine (**1**) a small amount of it must have been formed during the work-up, likely by methylation of alcohol (**2**) through *in situ* formed bromomethane. Thirdly, a mixture of different compounds and alcohol (**2**) (333 mg, *R_f* (CH₂Cl₂/MeOH, 95:5, *v/v*) = 0.22–0.07) was obtained. Purification of the third fraction by column chromatography (diameter = 4.5 cm, length = 33 cm) using CH₂Cl₂/MeOH (97.5:2.5, *v/v*) obtained alcohol (**2**) (291 mg, 1.55 mmol, 53%) as a pink solid. In Lang's pioneering work (Lang *et al.*, 1975), alcohol (**2**) was described as 'relatively unstable', a finding which we are unable to confirm – all the compounds isolated here remained stable in solid form at room temperature for over a year.

Analytical data of tetrazine (**1**): ¹H NMR (500 MHz, CDCl₃) δ [ppm]: 8.63 (*m*, 2H, *o*-C^{aryl}H), 7.67–7.57 (*m*, 3H, *m*-/*p*-C^{aryl}H), 5.10 (*s*, 2H, CH₂), 3.64 (*s*, 3H, CH₃). ¹³C{¹H}NMR (125 MHz{500 MHz}, CDCl₃) δ [ppm]: 166.3 (C^{aryl}CH₂), 165.2 (C^{aryl}Ph), 133.1 (*p*-C^{aryl}), 131.7 (C^{aryl} attached to tetrazine), 129.5 (*m*-C^{aryl}), 128.4 (*o*-C^{aryl}), 72.3 (CH₂), 59.8 (CH₃). MS (ESI, positive): *m/z* = 225.0 [C₁₀H₁₀N₄O+Na]⁺, 427.1 [2-(C₁₀H₁₀N₄O)+Na]⁺. *R_f* (CH₂Cl₂/MeOH, 95:5, *v/v*) = 0.25). Tetrazine (**1**) was crystallized by slow evaporation from a CH₂Cl₂/MeOH solution at room temperature.

Analytical data of alcohol (**2**): ¹H NMR (500 MHz, CDCl₃) δ [ppm]: 8.62 (*m*, 2H, *o*-C^{aryl}H), 7.66 (*m*, 1H, *p*-C^{aryl}H), 7.61 (*m*, 2H, *m*-C^{aryl}H), 5.34 (*d*, ³*J* = 6.2 Hz, 2H, CH₂), 3.12 (*t*, ³*J* = 6.3 Hz, 1H, OH). ¹³C{¹H}NMR (125 MHz{500 MHz}, CDCl₃)

δ [ppm]: 167.4 (C^{aryl}CH₂), 165.6 (C^{aryl}Ph), 133.2 (*p*-C^{aryl}), 131.6 (C^{aryl} attached to tetrazine), 129.5 (*m*-C^{aryl}), 128.4 (*o*-C^{aryl}), 63.0 (CH₂). MS (ESI, negative): *m/z* = 186.9 [C₉H₈N₄O–H][–]. *R_f* (CH₂Cl₂/MeOH, 97.5:2.5, *v/v*) = 0.20). Alcohol (**2**) was crystallized by slow evaporation from a CH₂Cl₂/cyclohexane solution at room temperature.

Analytical data of bromide (**3**): ¹H NMR (500 MHz, CDCl₃) δ [ppm]: 8.63 (*m*, 2H, *o*-C^{aryl}H), 7.66 (*m*, 1H, *p*-C^{aryl}H), 7.61 (*m*, 2H, *m*-C^{aryl}H), 5.00 (*s*, 2H, CH₂). ¹³C{¹H}NMR (125 MHz{500 MHz}, CDCl₃) δ [ppm]: 167.4 (C^{aryl}CH₂), 164.3 (C^{aryl}Ph), 133.4 (*p*-C^{aryl}), 131.4 (C^{aryl} attached to tetrazine), 129.6 (*m*-C^{aryl}), 128.6 (*o*-C^{aryl}), 27.8 (CH₂). MS (ESI): the compound was not ionisable. *R_f* (CH₂Cl₂/MeOH, 95:5, *v/v*) = 0.79. Bromide (**3**) was crystallized by slow evaporation from a CH₂Cl₂/MeOH solution at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarised in Table 2. All structures were refined using *NoSpherA2* (Kleemiss *et al.*, 2021), an implementation of non-spherical atom-form-factors in *OLEX2* (Dolomanov *et al.*, 2009). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically. *ORCA 5.0* (Neese, 2022) was used for quantum mechanical calculations. The *olex2_refinement_description* section of the CIF gives further details.

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Computing details

3-(Methoxymethyl)-6-phenyl-1,2,4,5-tetrazine (1)

Crystal data

C₁₀H₁₀N₄O
 $M_r = 202.22$
 Triclinic, $P\bar{1}$
 $a = 5.3147$ (4) Å
 $b = 7.4164$ (8) Å
 $c = 12.2277$ (8) Å
 $\alpha = 86.710$ (7)°
 $\beta = 79.913$ (6)°
 $\gamma = 78.920$ (8)°
 $V = 465.53$ (7) Å³

$Z = 2$
 $F(000) = 212.144$
 $D_x = 1.443$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3153 reflections
 $\theta = 2.8$ – 32.2 °
 $\mu = 0.10$ mm⁻¹
 $T = 100$ K
 Block, clear light red
 $0.52 \times 0.24 \times 0.18$ mm

Data collection

SuperNova, Single source at offset/far, Eos diffractometer
 Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source
 Mirror monochromator
 Detector resolution: 8.0951 pixels mm⁻¹
 ω scans
 Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2025)

$T_{\min} = 0.571$, $T_{\max} = 1.000$
 8849 measured reflections
 3058 independent reflections
 2256 reflections with $I \geq 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\max} = 32.5$ °, $\theta_{\min} = 1.7$ °
 $h = -7 \rightarrow 7$
 $k = -10 \rightarrow 10$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.061$
 $S = 1.09$
 3058 reflections
 166 parameters
 0 restraints

10 constraints
 Primary atom site location: dual
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0081P)^2 + 0.0348P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = -0.0002$
 $\Delta\rho_{\max} = 0.34$ e Å⁻³
 $\Delta\rho_{\min} = -0.33$ e Å⁻³

Special details

Refinement. Refinement using NoSpherA2, an implementation of NON-SPHERical Atom-form-factors in Olex2. The following options were used: SOFTWARE: ORCA 6.1 PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: r2SCAN BASIS SET: def2-TZVPP CHARGE: 0 MULTIPLICITY: 1 SOLVATION: Water DATE: 2026-09-01_14-23-46. Hydrogen atoms were refined isotropically.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.92532 (11)	0.72986 (10)	0.04592 (5)	0.01998 (16)
N1	0.90879 (13)	0.72470 (11)	0.29459 (5)	0.01504 (16)
N2	0.80917 (13)	0.68850 (11)	0.39730 (5)	0.01471 (16)
N3	0.40354 (13)	0.86997 (11)	0.37086 (5)	0.01404 (16)
N4	0.50426 (13)	0.90517 (11)	0.26685 (5)	0.01454 (16)
C1	0.88144 (18)	0.88087 (14)	0.11730 (7)	0.01780 (19)
H1A	1.0746 (17)	0.9105 (14)	0.1216 (7)	0.0214 (2)*
H1B	0.7597 (17)	0.9979 (14)	0.0836 (7)	0.0214 (2)*
C2	0.75552 (15)	0.83623 (13)	0.23290 (6)	0.01368 (17)
C3	0.55900 (15)	0.76548 (12)	0.43439 (6)	0.01153 (17)
C4	0.45400 (15)	0.73006 (12)	0.55162 (6)	0.01131 (17)
C5	0.61259 (15)	0.61944 (13)	0.61873 (6)	0.01317 (18)
H5	0.8094 (16)	0.5550 (13)	0.5846 (7)	0.0158 (2)*
C6	0.51547 (16)	0.58844 (13)	0.73007 (7)	0.01524 (18)
H6	0.6404 (16)	0.5014 (14)	0.7800 (7)	0.0183 (2)*
C7	0.26109 (16)	0.66712 (13)	0.77537 (7)	0.01518 (18)
H7	0.1901 (16)	0.6439 (13)	0.8630 (7)	0.0182 (2)*
C8	0.10211 (16)	0.77628 (13)	0.70835 (7)	0.01495 (18)
H8	−0.0982 (17)	0.8388 (14)	0.7428 (7)	0.0179 (2)*
C9	0.19769 (15)	0.80708 (13)	0.59684 (7)	0.01359 (18)
H9	0.0751 (16)	0.8899 (13)	0.5440 (7)	0.0163 (2)*
C10	0.6980 (2)	0.70573 (16)	0.00716 (8)	0.0244 (2)
H10A	0.7482 (19)	0.5807 (16)	−0.0412 (8)	0.0366 (3)*
H10B	0.5439 (19)	0.7009 (15)	0.0746 (8)	0.0366 (3)*
H10C	0.6313 (19)	0.8196 (16)	−0.0467 (8)	0.0366 (3)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0209 (3)	0.0204 (4)	0.0158 (3)	0.0008 (3)	0.0004 (2)	−0.0028 (3)
N1	0.0115 (3)	0.0168 (4)	0.0148 (3)	0.0001 (3)	0.0004 (3)	−0.0006 (3)
N2	0.0115 (3)	0.0165 (4)	0.0143 (3)	0.0009 (3)	−0.0012 (3)	0.0004 (3)
N3	0.0111 (3)	0.0158 (4)	0.0140 (3)	−0.0007 (3)	−0.0011 (3)	0.0007 (3)
N4	0.0132 (3)	0.0153 (4)	0.0137 (3)	−0.0005 (3)	−0.0014 (3)	0.0009 (3)
C1	0.0188 (4)	0.0172 (5)	0.0158 (4)	−0.0032 (4)	0.0011 (3)	0.0005 (4)
C2	0.0138 (4)	0.0131 (5)	0.0134 (4)	−0.0025 (3)	0.0000 (3)	−0.0005 (3)
C3	0.0103 (4)	0.0112 (4)	0.0130 (4)	−0.0019 (3)	−0.0018 (3)	−0.0007 (3)
C4	0.0102 (4)	0.0114 (4)	0.0123 (4)	−0.0019 (3)	−0.0015 (3)	−0.0007 (3)
C5	0.0114 (4)	0.0141 (5)	0.0134 (4)	−0.0010 (3)	−0.0018 (3)	−0.0006 (3)

C6	0.0142 (4)	0.0175 (5)	0.0135 (4)	−0.0018 (4)	−0.0025 (3)	0.0006 (3)
C7	0.0152 (4)	0.0167 (5)	0.0129 (4)	−0.0029 (4)	−0.0003 (3)	−0.0011 (3)
C8	0.0124 (4)	0.0167 (5)	0.0146 (4)	−0.0023 (4)	0.0008 (3)	−0.0014 (3)
C9	0.0108 (4)	0.0152 (5)	0.0140 (4)	−0.0011 (3)	−0.0017 (3)	−0.0001 (3)
C10	0.0280 (5)	0.0250 (6)	0.0199 (5)	−0.0030 (5)	−0.0043 (4)	−0.0032 (4)

Geometric parameters (Å, °)

O1—C1	1.4181 (11)	C4—C9	1.4003 (11)
O1—C10	1.4176 (11)	C5—H5	1.084 (8)
N1—N2	1.3087 (9)	C5—C6	1.3915 (11)
N1—C2	1.3422 (10)	C6—H6	1.078 (8)
N2—C3	1.3514 (10)	C6—C7	1.3952 (11)
N3—N4	1.3226 (9)	C7—H7	1.087 (9)
N3—C3	1.3403 (10)	C7—C8	1.3944 (11)
N4—C2	1.3359 (10)	C8—H8	1.096 (8)
C1—H1A	1.101 (9)	C8—C9	1.3912 (11)
C1—H1B	1.086 (9)	C9—H9	1.081 (8)
C1—C2	1.5019 (12)	C10—H10A	1.092 (11)
C3—C4	1.4724 (11)	C10—H10B	1.060 (10)
C4—C5	1.3986 (11)	C10—H10C	1.084 (11)
C10—O1—C1	113.11 (7)	C6—C5—C4	119.78 (7)
C2—N1—N2	117.77 (7)	C6—C5—H5	119.5 (4)
C3—N2—N1	118.01 (7)	H6—C6—C5	118.5 (5)
C3—N3—N4	117.89 (6)	C7—C6—C5	120.50 (8)
C2—N4—N3	117.60 (7)	C7—C6—H6	121.0 (5)
H1A—C1—O1	106.1 (5)	H7—C7—C6	119.4 (4)
H1B—C1—O1	109.8 (5)	C8—C7—C6	119.77 (8)
H1B—C1—H1A	111.3 (7)	C8—C7—H7	120.8 (4)
C2—C1—O1	112.18 (8)	H8—C8—C7	120.5 (5)
C2—C1—H1A	108.1 (5)	C9—C8—C7	119.99 (8)
C2—C1—H1B	109.4 (5)	C9—C8—H8	119.5 (5)
N4—C2—N1	124.67 (8)	C8—C9—C4	120.29 (8)
C1—C2—N1	115.93 (7)	H9—C9—C4	119.2 (5)
C1—C2—N4	119.39 (7)	H9—C9—C8	120.5 (5)
N3—C3—N2	123.89 (7)	H10A—C10—O1	107.4 (5)
C4—C3—N2	117.22 (7)	H10B—C10—O1	110.6 (5)
C4—C3—N3	118.89 (7)	H10B—C10—H10A	112.8 (9)
C5—C4—C3	119.64 (7)	H10C—C10—O1	111.3 (6)
C9—C4—C3	120.71 (7)	H10C—C10—H10A	108.2 (7)
C9—C4—C5	119.65 (7)	H10C—C10—H10B	106.6 (8)
H5—C5—C4	120.7 (4)		
O1—C1—C2—N1	73.17 (8)	N4—N3—C3—C4	177.76 (7)
O1—C1—C2—N4	−105.80 (8)	C2—N1—N2—C3	0.06 (9)
N1—N2—C3—N3	3.10 (9)	C2—N4—N3—C3	−1.00 (9)
N1—N2—C3—C4	−177.26 (7)	C2—C1—O1—C10	78.41 (9)

N1—C2—N4—N3	4.28 (11)	C3—C4—C5—C6	178.83 (8)
N2—N1—C2—N4	−3.79 (9)	C3—C4—C9—C8	−178.51 (8)
N2—N1—C2—C1	177.30 (8)	C4—C5—C6—C7	−0.10 (10)
N2—C3—N3—N4	−2.60 (10)	C4—C9—C8—C7	−0.51 (10)
N2—C3—C4—C5	−0.45 (9)	C5—C4—C9—C8	1.00 (10)
N2—C3—C4—C9	179.06 (8)	C5—C6—C7—C8	0.59 (11)
N3—N4—C2—C1	−176.84 (8)	C6—C5—C4—C9	−0.69 (10)
N3—C3—C4—C5	179.21 (8)	C6—C7—C8—C9	−0.29 (11)
N3—C3—C4—C9	−1.28 (10)		

(6-Phenyl-1,2,4,5-tetrazin-3-yl)methanol (2)*Crystal data*C₉H₈N₄O $M_r = 188.19$ Monoclinic, $P2_1/n$ $a = 11.8719$ (3) Å $b = 8.4682$ (2) Å $c = 17.2987$ (5) Å $\beta = 92.709$ (2)° $V = 1737.16$ (8) Å³ $Z = 8$ $F(000) = 784.550$ $D_x = 1.439$ Mg m^{−3}Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9457 reflections

 $\theta = 2.1$ – 30.8° $\mu = 0.10$ mm^{−1} $T = 100$ K

Needle, clear red

 $0.35 \times 0.09 \times 0.06$ mm*Data collection*

SuperNova, Single source at offset/far, Eos diffractometer

Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source

Mirror monochromator

Detector resolution: 8.0951 pixels mm^{−1} ω scans

Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2025)

 $T_{\min} = 0.744$, $T_{\max} = 1.000$

32315 measured reflections

4666 independent reflections

3774 reflections with $I \geq 2\sigma(I)$ $R_{\text{int}} = 0.045$ $\theta_{\max} = 29.1^\circ$, $\theta_{\min} = 2.0^\circ$ $h = -16 \rightarrow 17$ $k = -12 \rightarrow 11$ $l = -24 \rightarrow 24$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.030$ $wR(F^2) = 0.066$ $S = 1.07$

4666 reflections

317 parameters

0 restraints

0 constraints

Primary atom site location: dual

All H-atom parameters refined

 $w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 0.2291P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = -0.0000$ $\Delta\rho_{\max} = 0.21$ e Å^{−3} $\Delta\rho_{\min} = -0.21$ e Å^{−3}*Special details*

Refinement. Refinement using NoSpherA2, an implementation of NON-SPHERical Atom-form-factors in Olex2. The following options were used: SOFTWARE: ORCA 6.1 PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: r2SCAN BASIS SET: def2-TZVPP CHARGE: 0 MULTIPLICITY: 1 SOLVATION: Water DATE: 2026-09-01_16-19-35. Hydrogen atoms were refined isotropically.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1A	0.59801 (5)	1.02413 (7)	0.28063 (4)	0.01965 (14)

H1A	0.6607 (10)	0.9789 (14)	0.3110 (7)	0.029 (3)*
O1B	0.86881 (5)	1.01966 (7)	0.25962 (4)	0.02058 (14)
H1B	0.8062 (11)	0.9790 (15)	0.2273 (7)	0.035 (3)*
N1A	0.52904 (6)	0.74303 (8)	0.12699 (4)	0.01679 (15)
N1B	0.76371 (6)	0.82834 (8)	0.36380 (4)	0.01715 (15)
N2A	0.57676 (5)	0.67508 (8)	0.06899 (4)	0.01688 (15)
N2B	0.71656 (6)	0.75248 (8)	0.42088 (4)	0.01752 (15)
N3A	0.75136 (6)	0.79518 (8)	0.10707 (4)	0.01599 (15)
N3B	0.89047 (6)	0.62307 (9)	0.45041 (4)	0.01907 (16)
N4A	0.70263 (6)	0.86196 (8)	0.16591 (4)	0.01601 (15)
N4B	0.93624 (6)	0.69768 (9)	0.39344 (4)	0.01918 (16)
C1A	0.53859 (7)	0.89889 (11)	0.24476 (5)	0.01957 (18)
H1Aa	0.5285 (9)	0.8000 (13)	0.2849 (6)	0.039 (3)*
H1Ab	0.4555 (9)	0.9394 (13)	0.2265 (6)	0.043 (3)*
C1B	0.92960 (7)	0.88877 (11)	0.28883 (5)	0.01941 (18)
H1Ba	0.9452 (9)	0.8015 (13)	0.2444 (6)	0.042 (3)*
H1Bb	1.0106 (9)	0.9282 (12)	0.3117 (6)	0.034 (3)*
C2A	0.59403 (6)	0.83232 (9)	0.17545 (5)	0.01452 (16)
C2B	0.87263 (7)	0.80304 (10)	0.35268 (5)	0.01583 (17)
C3A	0.68812 (6)	0.70005 (9)	0.06061 (5)	0.01377 (16)
C3B	0.78189 (7)	0.65559 (10)	0.46492 (5)	0.01512 (17)
C4A	0.74238 (6)	0.61986 (9)	−0.00351 (5)	0.01426 (16)
C4B	0.73344 (7)	0.57847 (10)	0.53216 (5)	0.01579 (17)
C5A	0.67944 (7)	0.52052 (10)	−0.05393 (5)	0.01702 (17)
H5A	0.5903 (8)	0.5023 (12)	−0.0456 (6)	0.031 (3)*
C5B	0.61878 (7)	0.59683 (11)	0.54546 (5)	0.02024 (18)
H5B	0.5665 (9)	0.6653 (14)	0.5054 (6)	0.040 (3)*
C6A	0.73229 (7)	0.44423 (10)	−0.11365 (5)	0.01900 (18)
H6A	0.6838 (9)	0.3643 (13)	−0.1510 (6)	0.036 (3)*
C6B	0.57384 (8)	0.52971 (11)	0.61061 (5)	0.0245 (2)
H6B	0.4841 (9)	0.5440 (13)	0.6203 (6)	0.039 (3)*
C7A	0.84716 (7)	0.46702 (11)	−0.12364 (5)	0.01942 (18)
H7A	0.8874 (9)	0.4069 (13)	−0.1685 (7)	0.043 (3)*
C7B	0.64302 (8)	0.44385 (12)	0.66256 (5)	0.0257 (2)
H7B	0.6084 (9)	0.3926 (13)	0.7137 (7)	0.041 (3)*
C8A	0.90950 (7)	0.56615 (11)	−0.07371 (5)	0.01958 (18)
H8A	0.9988 (9)	0.5834 (13)	−0.0805 (6)	0.038 (3)*
C8B	0.75664 (8)	0.42286 (11)	0.64873 (5)	0.0247 (2)
H8B	0.8100 (9)	0.3533 (14)	0.6870 (7)	0.048 (3)*
C9A	0.85757 (7)	0.64189 (10)	−0.01341 (5)	0.01796 (18)
H9A	0.9041 (8)	0.7182 (12)	0.0273 (6)	0.028 (3)*
C9B	0.80233 (7)	0.48971 (10)	0.58373 (5)	0.01967 (18)
H9B	0.8907 (9)	0.4737 (13)	0.5731 (6)	0.039 (3)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0218 (3)	0.0163 (3)	0.0205 (3)	0.0027 (2)	−0.0014 (3)	−0.0006 (2)

O1B	0.0229 (3)	0.0159 (3)	0.0225 (3)	−0.0039 (2)	−0.0036 (3)	−0.0006 (2)
N1A	0.0115 (3)	0.0197 (4)	0.0190 (4)	−0.0028 (3)	−0.0002 (3)	−0.0001 (3)
N1B	0.0151 (3)	0.0180 (4)	0.0182 (4)	0.0037 (3)	−0.0015 (3)	0.0009 (3)
N2A	0.0120 (3)	0.0199 (4)	0.0187 (4)	−0.0036 (3)	−0.0004 (3)	−0.0019 (3)
N2B	0.0140 (3)	0.0197 (4)	0.0188 (4)	0.0044 (3)	−0.0006 (3)	0.0011 (3)
N3A	0.0125 (3)	0.0189 (4)	0.0164 (4)	−0.0045 (3)	−0.0005 (3)	−0.0008 (3)
N3B	0.0149 (3)	0.0211 (4)	0.0210 (4)	0.0054 (3)	−0.0016 (3)	0.0015 (3)
N4A	0.0145 (3)	0.0174 (4)	0.0160 (3)	−0.0038 (3)	−0.0006 (3)	−0.0005 (3)
N4B	0.0145 (3)	0.0215 (4)	0.0215 (4)	0.0035 (3)	−0.0000 (3)	0.0010 (3)
C1A	0.0161 (4)	0.0211 (5)	0.0217 (5)	0.0003 (3)	0.0019 (3)	−0.0022 (4)
C1B	0.0196 (4)	0.0174 (4)	0.0212 (5)	−0.0018 (3)	0.0007 (3)	−0.0013 (3)
C2A	0.0132 (4)	0.0141 (4)	0.0162 (4)	−0.0005 (3)	−0.0003 (3)	0.0010 (3)
C2B	0.0146 (4)	0.0154 (4)	0.0173 (4)	0.0007 (3)	−0.0012 (3)	−0.0018 (3)
C3A	0.0117 (4)	0.0151 (4)	0.0144 (4)	−0.0025 (3)	−0.0008 (3)	0.0015 (3)
C3B	0.0141 (4)	0.0151 (4)	0.0160 (4)	0.0020 (3)	−0.0014 (3)	−0.0018 (3)
C4A	0.0131 (4)	0.0156 (4)	0.0139 (4)	−0.0026 (3)	−0.0009 (3)	0.0015 (3)
C4B	0.0166 (4)	0.0149 (4)	0.0157 (4)	0.0011 (3)	−0.0013 (3)	−0.0017 (3)
C5A	0.0152 (4)	0.0197 (4)	0.0160 (4)	−0.0035 (3)	−0.0009 (3)	−0.0005 (3)
C5B	0.0176 (4)	0.0230 (5)	0.0202 (5)	0.0023 (3)	0.0013 (3)	−0.0010 (4)
C6A	0.0198 (4)	0.0207 (4)	0.0164 (4)	−0.0035 (3)	−0.0003 (3)	−0.0017 (3)
C6B	0.0234 (5)	0.0287 (5)	0.0217 (5)	−0.0027 (4)	0.0048 (4)	−0.0015 (4)
C7A	0.0201 (4)	0.0219 (4)	0.0165 (4)	0.0002 (3)	0.0029 (3)	−0.0004 (3)
C7B	0.0320 (5)	0.0267 (5)	0.0183 (5)	−0.0086 (4)	0.0015 (4)	0.0006 (4)
C8A	0.0147 (4)	0.0245 (5)	0.0196 (4)	−0.0009 (3)	0.0022 (3)	−0.0002 (3)
C8B	0.0289 (5)	0.0243 (5)	0.0203 (5)	−0.0049 (4)	−0.0057 (4)	0.0039 (4)
C9A	0.0134 (4)	0.0221 (4)	0.0183 (4)	−0.0030 (3)	0.0002 (3)	−0.0010 (3)
C9B	0.0201 (4)	0.0194 (4)	0.0190 (4)	−0.0005 (3)	−0.0043 (3)	0.0012 (3)

Geometric parameters (Å, °)

O1A—H1A	0.969 (12)	C3B—C4B	1.4742 (12)
O1A—C1A	1.4022 (10)	C4A—C5A	1.4018 (11)
O1B—H1B	0.972 (13)	C4A—C9A	1.3988 (11)
O1B—C1B	1.4036 (10)	C4B—C5B	1.3999 (11)
N1A—N2A	1.3086 (10)	C4B—C9B	1.4003 (11)
N1A—C2A	1.3448 (10)	C5A—H5A	1.085 (10)
N1B—N2B	1.3242 (10)	C5A—C6A	1.3926 (12)
N1B—C2B	1.3336 (10)	C5B—H5B	1.078 (11)
N2A—C3A	1.3534 (10)	C5B—C6B	1.3909 (13)
N2B—C3B	1.3413 (10)	C6A—H6A	1.082 (10)
N3A—N4A	1.3214 (10)	C6A—C7A	1.3961 (12)
N3A—C3A	1.3421 (10)	C6B—H6B	1.093 (11)
N3B—N4B	1.3101 (10)	C6B—C7B	1.3932 (13)
N3B—C3B	1.3533 (10)	C7A—H7A	1.061 (11)
N4A—C2A	1.3314 (10)	C7A—C8A	1.3922 (12)
N4B—C2B	1.3466 (10)	C7B—H7B	1.084 (11)
C1A—H1Aa	1.098 (11)	C7B—C8B	1.3925 (13)
C1A—H1Ab	1.078 (11)	C8A—H8A	1.082 (10)

C1A—C2A	1.5042 (12)	C8A—C9A	1.3929 (12)
C1B—H1Ba	1.089 (11)	C8B—H8B	1.071 (11)
C1B—H1Bb	1.075 (10)	C8B—C9B	1.3918 (13)
C1B—C2B	1.5083 (12)	C9A—H9A	1.087 (10)
C3A—C4A	1.4745 (11)	C9B—H9B	1.082 (11)
C1A—O1A—H1A	107.3 (7)	C9A—C4A—C3A	119.68 (7)
C1B—O1B—H1B	107.0 (7)	C9A—C4A—C5A	119.95 (8)
C2A—N1A—N2A	117.96 (7)	C5B—C4B—C3B	119.95 (7)
C2B—N1B—N2B	118.46 (7)	C9B—C4B—C3B	120.17 (7)
C3A—N2A—N1A	118.29 (7)	C9B—C4B—C5B	119.87 (8)
C3B—N2B—N1B	117.83 (7)	H5A—C5A—C4A	119.8 (5)
C3A—N3A—N4A	117.73 (7)	C6A—C5A—C4A	119.63 (8)
C3B—N3B—N4B	118.29 (7)	C6A—C5A—H5A	120.6 (5)
C2A—N4A—N3A	118.46 (7)	H5B—C5B—C4B	119.3 (6)
C2B—N4B—N3B	118.11 (7)	C6B—C5B—C4B	120.07 (8)
H1Aa—C1A—O1A	111.4 (6)	C6B—C5B—H5B	120.6 (6)
H1Ab—C1A—O1A	108.9 (6)	H6A—C6A—C5A	119.1 (6)
H1Ab—C1A—H1Aa	107.6 (8)	C7A—C6A—C5A	120.31 (8)
C2A—C1A—O1A	113.97 (7)	C7A—C6A—H6A	120.5 (6)
C2A—C1A—H1Aa	106.4 (6)	H6B—C6B—C5B	119.6 (6)
C2A—C1A—H1Ab	108.3 (6)	C7B—C6B—C5B	119.93 (9)
H1Ba—C1B—O1B	112.6 (6)	C7B—C6B—H6B	120.5 (6)
H1Bb—C1B—O1B	108.8 (6)	H7A—C7A—C6A	120.0 (6)
H1Bb—C1B—H1Ba	106.9 (8)	C8A—C7A—C6A	120.02 (8)
C2B—C1B—O1B	113.76 (7)	C8A—C7A—H7A	119.9 (6)
C2B—C1B—H1Ba	106.7 (6)	H7B—C7B—C6B	120.1 (6)
C2B—C1B—H1Bb	107.7 (6)	C8B—C7B—C6B	120.14 (9)
N4A—C2A—N1A	123.99 (8)	C8B—C7B—H7B	119.8 (6)
C1A—C2A—N1A	116.60 (7)	H8A—C8A—C7A	120.6 (6)
C1A—C2A—N4A	119.40 (7)	C9A—C8A—C7A	120.08 (8)
N4B—C2B—N1B	123.68 (8)	C9A—C8A—H8A	119.3 (6)
C1B—C2B—N1B	119.98 (7)	H8B—C8B—C7B	120.9 (6)
C1B—C2B—N4B	116.27 (7)	C9B—C8B—C7B	120.31 (9)
N3A—C3A—N2A	123.45 (8)	C9B—C8B—H8B	118.8 (6)
C4A—C3A—N2A	118.18 (7)	C8A—C9A—C4A	120.01 (8)
C4A—C3A—N3A	118.36 (7)	H9A—C9A—C4A	118.0 (5)
N3B—C3B—N2B	123.33 (8)	H9A—C9A—C8A	122.0 (5)
C4B—C3B—N2B	118.84 (7)	C8B—C9B—C4B	119.66 (8)
C4B—C3B—N3B	117.83 (7)	H9B—C9B—C4B	120.0 (6)
C5A—C4A—C3A	120.37 (7)	H9B—C9B—C8B	120.3 (6)
O1A—C1A—C2A—N1A	−162.92 (7)	N3B—C3B—C4B—C5B	−174.15 (7)
O1A—C1A—C2A—N4A	18.03 (9)	N3B—C3B—C4B—C9B	7.26 (9)
O1B—C1B—C2B—N1B	16.06 (9)	N4A—N3A—C3A—C4A	−177.69 (7)
O1B—C1B—C2B—N4B	−166.93 (7)	N4B—N3B—C3B—C4B	−176.25 (7)
N1A—N2A—C3A—N3A	−2.39 (9)	C2A—N1A—N2A—C3A	−0.78 (9)
N1A—N2A—C3A—C4A	178.34 (7)	C2A—N4A—N3A—C3A	−0.49 (8)

N1A—C2A—N4A—N3A	−2.73 (9)	C2B—N1B—N2B—C3B	0.77 (9)
N1B—N2B—C3B—N3B	−5.01 (9)	C2B—N4B—N3B—C3B	0.23 (9)
N1B—N2B—C3B—C4B	175.76 (7)	C3A—C4A—C5A—C6A	−179.25 (8)
N1B—C2B—N4B—N3B	−4.47 (10)	C3A—C4A—C9A—C8A	179.81 (8)
N2A—N1A—C2A—N4A	3.38 (9)	C3B—C4B—C5B—C6B	−177.30 (8)
N2A—N1A—C2A—C1A	−175.62 (7)	C3B—C4B—C9B—C8B	177.35 (8)
N2A—C3A—N3A—N4A	3.04 (9)	C4A—C5A—C6A—C7A	−0.35 (10)
N2A—C3A—C4A—C5A	−0.12 (9)	C4A—C9A—C8A—C7A	−0.75 (10)
N2A—C3A—C4A—C9A	−179.41 (7)	C4B—C5B—C6B—C7B	−0.14 (10)
N2B—N1B—C2B—N4B	3.95 (9)	C4B—C9B—C8B—C7B	0.03 (10)
N2B—N1B—C2B—C1B	−179.28 (7)	C5A—C4A—C9A—C8A	0.51 (9)
N2B—C3B—N3B—N4B	4.50 (9)	C5A—C6A—C7A—C8A	0.12 (10)
N2B—C3B—C4B—C5B	5.13 (9)	C5B—C4B—C9B—C8B	−1.23 (9)
N2B—C3B—C4B—C9B	−173.46 (8)	C5B—C6B—C7B—C8B	−1.07 (11)
N3A—N4A—C2A—C1A	176.25 (7)	C6A—C5A—C4A—C9A	0.04 (10)
N3A—C3A—C4A—C5A	−179.42 (7)	C6A—C7A—C8A—C9A	0.43 (10)
N3A—C3A—C4A—C9A	1.29 (9)	C6B—C5B—C4B—C9B	1.29 (10)
N3B—N4B—C2B—C1B	178.65 (7)	C6B—C7B—C8B—C9B	1.13 (11)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1A—H1A···N1B	0.969 (12)	1.963 (13)	2.9019 (9)	162.7 (10)
O1B—H1B···N4A	0.972 (13)	1.871 (13)	2.8287 (9)	168.2 (11)

3-(Bromomethyl)-6-phenyl-1,2,4,5-tetrazine (3)*Crystal data*C₉H₇BrN₄*M_r* = 251.09Triclinic, *P*1*a* = 5.2376 (4) Å*b* = 7.5069 (6) Å*c* = 12.0638 (8) Å*α* = 89.632 (6)°*β* = 80.517 (6)°*γ* = 79.451 (7)°*V* = 459.80 (6) Å³*Z* = 2*F*(000) = 247.736*D_x* = 1.814 Mg m^{−3}Mo *Kα* radiation, *λ* = 0.71073 Å

Cell parameters from 3207 reflections

θ = 3.2–30.6°*μ* = 4.44 mm^{−1}*T* = 100 K

Block, clear red

0.35 × 0.29 × 0.09 mm

Data collection

SuperNova, Single source at offset/far, Eos diffractometer

Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source

Mirror monochromator

Detector resolution: 8.0951 pixels mm^{−1}*ω* scans

Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2025)

T_{min} = 0.394, *T_{max}* = 1.000

7431 measured reflections

2531 independent reflections

2136 reflections with *I* ≥ 2*σ*(*I*)*R_{int}* = 0.048*θ_{max}* = 29.6°, *θ_{min}* = 1.7°*h* = −7→7*k* = −10→10*l* = −17→16

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.033$ $wR(F^2) = 0.061$ $S = 1.03$

2531 reflections

148 parameters

0 restraints

7 constraints

Primary atom site location: dual

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0159P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = -0.0002$ $\Delta\rho_{\max} = 0.81 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.70 \text{ e } \text{\AA}^{-3}$ *Special details*

Refinement. Refinement using NoSpherA2, an implementation of NON-SPHERICAL Atom-form-factors in Olex2. The following options were used: SOFTWARE: ORCA 6.1 PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: r2SCAN BASIS SET: def2-TZVPP CHARGE: 0 MULTIPLICITY: 1 SOLVATION: Water DATE: 2026-09-01_14-39-25. Hydrogen atoms were refined isotropically.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.65100 (5)	0.72768 (3)	0.010906 (19)	0.02391 (8)
N1	0.8794 (3)	0.7258 (3)	0.28825 (15)	0.0176 (4)
N2	0.7978 (3)	0.6944 (3)	0.39466 (15)	0.0178 (4)
N3	0.3775 (3)	0.8719 (2)	0.38276 (15)	0.0172 (4)
N4	0.4589 (3)	0.9025 (3)	0.27664 (16)	0.0191 (4)
C1	0.8027 (5)	0.8656 (3)	0.11273 (19)	0.0212 (5)
H1a	1.023 (5)	0.823 (3)	0.0968 (19)	0.0254 (6)*
H1b	0.726 (5)	1.015 (3)	0.097 (2)	0.0254 (6)*
C2	0.7078 (4)	0.8275 (3)	0.23224 (18)	0.0159 (4)
C3	0.5477 (4)	0.7671 (3)	0.43979 (18)	0.0144 (4)
C4	0.4543 (4)	0.7315 (3)	0.55885 (17)	0.0134 (4)
C5	0.6212 (4)	0.6175 (3)	0.62007 (18)	0.0148 (4)
H5	0.817 (4)	0.550 (3)	0.5826 (18)	0.0178 (5)*
C6	0.5325 (4)	0.5841 (3)	0.73262 (19)	0.0174 (5)
H6	0.664 (4)	0.495 (3)	0.7779 (19)	0.0209 (5)*
C7	0.2781 (4)	0.6636 (3)	0.78360 (19)	0.0171 (5)
H7	0.211 (4)	0.629 (3)	0.8726 (19)	0.0205 (5)*
C8	0.1121 (4)	0.7774 (3)	0.72290 (19)	0.0178 (5)
H8	-0.086 (4)	0.841 (3)	0.7634 (19)	0.0214 (5)*
C9	0.1997 (4)	0.8101 (3)	0.61046 (18)	0.0152 (4)
H9	0.075 (4)	0.900 (3)	0.5609 (19)	0.0182 (5)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02876 (14)	0.02440 (14)	0.01709 (13)	-0.00081 (10)	-0.00401 (9)	-0.00149 (9)
N1	0.0139 (9)	0.0189 (10)	0.0180 (10)	0.0008 (7)	-0.0008 (7)	-0.0004 (8)
N2	0.0124 (9)	0.0200 (10)	0.0189 (10)	0.0018 (8)	-0.0022 (7)	0.0004 (8)
N3	0.0134 (9)	0.0171 (10)	0.0194 (10)	0.0015 (7)	-0.0024 (7)	0.0004 (8)
N4	0.0159 (10)	0.0192 (10)	0.0205 (10)	0.0012 (8)	-0.0030 (7)	0.0022 (8)
C1	0.0201 (12)	0.0232 (13)	0.0195 (12)	-0.0036 (10)	-0.0020 (9)	0.0040 (10)

C2	0.0149 (11)	0.0156 (11)	0.0171 (11)	−0.0015 (8)	−0.0036 (8)	0.0004 (9)
C3	0.0116 (10)	0.0135 (11)	0.0180 (11)	−0.0010 (8)	−0.0032 (8)	−0.0010 (9)
C4	0.0121 (10)	0.0098 (10)	0.0183 (11)	−0.0003 (8)	−0.0041 (8)	−0.0015 (8)
C5	0.0114 (10)	0.0134 (11)	0.0181 (11)	0.0019 (8)	−0.0023 (8)	−0.0008 (9)
C6	0.0145 (11)	0.0153 (11)	0.0214 (12)	0.0012 (9)	−0.0045 (9)	−0.0006 (9)
C7	0.0166 (11)	0.0153 (11)	0.0186 (12)	−0.0013 (9)	−0.0023 (9)	0.0012 (9)
C8	0.0129 (11)	0.0181 (12)	0.0206 (12)	0.0003 (9)	−0.0008 (9)	−0.0009 (9)
C9	0.0115 (10)	0.0152 (11)	0.0179 (11)	−0.0000 (8)	−0.0021 (8)	0.0004 (9)

Geometric parameters (Å, °)

Br1—C1	1.962 (2)	C4—C5	1.404 (3)
N1—N2	1.318 (2)	C4—C9	1.399 (3)
N1—C2	1.338 (3)	C5—H5	1.09 (2)
N2—C3	1.348 (3)	C5—C6	1.397 (3)
N3—N4	1.314 (2)	C6—H6	1.08 (2)
N3—C3	1.351 (3)	C6—C7	1.397 (3)
N4—C2	1.345 (3)	C7—H7	1.12 (2)
C1—H1a	1.13 (2)	C7—C8	1.397 (3)
C1—H1b	1.15 (3)	C8—H8	1.09 (2)
C1—C2	1.489 (3)	C8—C9	1.394 (3)
C3—C4	1.478 (3)	C9—H9	1.10 (2)
C2—N1—N2	117.68 (17)	C9—C4—C3	120.19 (18)
C3—N2—N1	117.92 (17)	C9—C4—C5	119.94 (19)
C3—N3—N4	118.14 (18)	H5—C5—C4	122.4 (11)
C2—N4—N3	117.46 (18)	C6—C5—C4	119.76 (19)
H1a—C1—Br1	109.3 (12)	C6—C5—H5	117.8 (11)
H1b—C1—Br1	105.8 (12)	H6—C6—C5	118.5 (12)
H1b—C1—H1a	115.0 (17)	C7—C6—C5	119.9 (2)
C2—C1—Br1	110.83 (15)	C7—C6—H6	121.6 (12)
C2—C1—H1a	107.5 (12)	H7—C7—C6	118.0 (12)
C2—C1—H1b	108.4 (12)	C8—C7—C6	120.4 (2)
N4—C2—N1	125.0 (2)	C8—C7—H7	121.5 (12)
C1—C2—N1	117.44 (19)	H8—C8—C7	120.2 (12)
C1—C2—N4	117.57 (19)	C9—C8—C7	119.8 (2)
N3—C3—N2	123.82 (19)	C9—C8—H8	120.0 (12)
C4—C3—N2	118.23 (18)	C8—C9—C4	120.18 (19)
C4—C3—N3	117.95 (18)	H9—C9—C4	118.2 (12)
C5—C4—C3	119.87 (18)	H9—C9—C8	121.6 (12)
Br1—C1—C2—N1	107.43 (16)	N3—C3—C4—C9	−2.1 (2)
Br1—C1—C2—N4	−74.63 (17)	N4—N3—C3—C4	−179.36 (18)
N1—N2—C3—N3	−0.9 (2)	C2—N1—N2—C3	−0.2 (2)
N1—N2—C3—C4	179.59 (18)	C2—N4—N3—C3	−0.3 (2)
N1—C2—N4—N3	−0.8 (2)	C3—C4—C5—C6	179.94 (19)
N2—N1—C2—N4	1.0 (2)	C3—C4—C9—C8	−179.63 (19)
N2—N1—C2—C1	178.79 (19)	C4—C5—C6—C7	0.3 (2)

N2—C3—N3—N4	1.1 (2)	C4—C9—C8—C7	−0.9 (2)
N2—C3—C4—C5	−2.9 (2)	C5—C4—C9—C8	0.7 (2)
N2—C3—C4—C9	177.44 (19)	C5—C6—C7—C8	−0.5 (2)
N3—N4—C2—C1	−178.56 (19)	C6—C5—C4—C9	−0.4 (2)
N3—C3—C4—C5	177.48 (18)	C6—C7—C8—C9	0.8 (2)
