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An independent refinement of H-atom coordinates from laboratory X-ray powder data in tetraformaltrisazine

Dmitry V. Albov,[a]* Adnan Jassem[b] and Anatoly I. Kuznetsov[b]

[a]Department of Chemistry, Moscow State University, 119992 Moscow, Russian Federation, and [b]Lomonosov State Academy of Fine Chemical Technology, Prospekt Vernadskogo 86, 117571 Moscow, Russian Federation

Correspondence e-mail: albov@struct.chem.msu.ru

Key indicators

Powder X-ray study
T = 298 K
Mean σ(N–N) = 0.009 Å
R factor = 0.025
wR factor = 0.008

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

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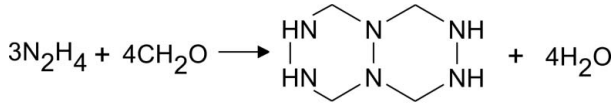
The structure of centrosymmetric tetraformaltrisazine (systematic name: 1,2,3,4,5,6,7,8-octahydro-1,2,4,5-tetrazino-[1,2-*a*][1,2,4,5]tetrazine), $C_4H_{12}N_6$, has been solved by simulated annealing from X-ray laboratory powder data and refined by Rietveld refinement without any restraints for non-H atoms. The coordinates of H atoms forming hydrogen bonds were refined independently. Tetraformaltrisazine can be used as a biologically active compound.

Comment

The condensation of formaldehyde with hydrazine may lead to different products. One of the most easily obtainable is tetraformaltrisazine, (I) (Neureiter, 1959). For further study of this compound, the structure of the molecule needs to be known. Since we failed to obtain a single crystal of (I), the structure was determined using X-ray powder techniques.



(I)

It is evident (Fig. 1) that tetraformaltrisazine is a hexaaza-derivative of decalin, in which all four H atoms attached to N atoms are in axial positions, forming eight hydrogen bonds around one molecule (Fig. 2 and Table 2). The molecule has a centre of symmetry.

Experimental

Paraformaldehyde (12 g, 0.4 mol) was added slowly to hydrazine hydrate (15 g, 0.3 mol) with cooling and stirring. Stirring was continued for 20 min at room temperature, and then the reaction mixture was left to stand at room temperature for 2 d. The mixture was filtered and the precipitate was washed with hot propan-2-ol (yield 8 g, 56%; m.p. 488–490 K). Analysis found: C 32.80, H 8.27, N 57.28%; $C_4H_{12}N_6$ requires: C 33.31, H 8.40, N 58.28%. ^{1}H NMR (D_2O, 250 MHz, δ, p.p.m.): 3.6 (*s*), 3.9 (*s*) (4H, NH); 4.1 (*s*), 4.9 (*s*) (8H, CH_2).

Crystal data

$C_4H_{12}N_6$
M_r = 144.20
Monoclinic, $P2_1/n$
a = 6.3243 (4) Å
b = 4.8633 (3) Å
c = 11.3322 (9) Å
β = 92.042 (14)°
V = 348.32 (4) Å^3
Z = 2
D_x = 1.375 Mg m^{-3}
Cu $K\alpha_1$ radiation
μ = 0.81 mm^{-1}
Specimen shape: flat sheet
15 × 15 × 0.5 mm
Specimen prepared at 298 K
Particle morphology: lump-like, colourless

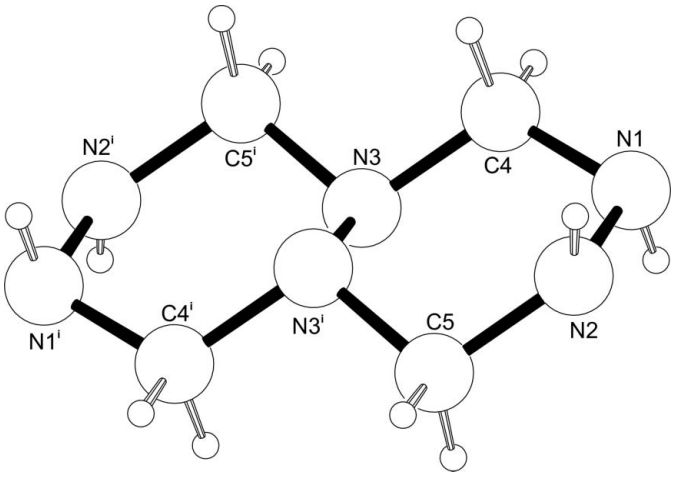


Figure 1
PLATON (Spek, 2003) view of the title compound, with the atom-numbering scheme. Symmetry code as in Table 1.

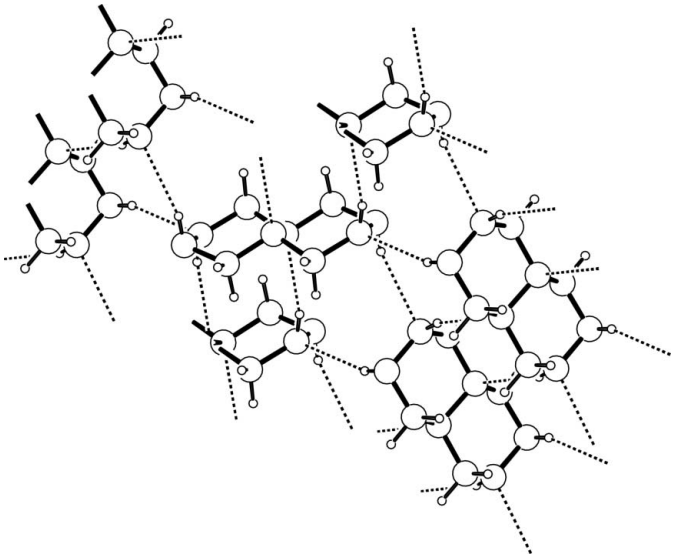


Figure 2
Hydrogen bonds (dashed lines) in the packing of the title compound.

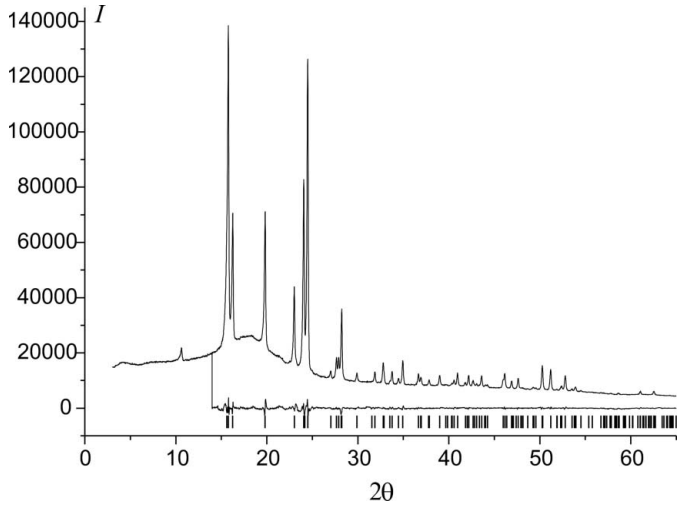


Figure 3
Rietveld plot for the title compound. The upper trace is the observed profile and the lower trace is the difference between observed and calculated; indexed lines are shown with dashes.

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.440 (15)	N3—C4	1.489 (9)
N1—C4	1.432 (9)	N3—N3^{i}	1.484 (9)
N2—C5	1.474 (9)	C5—N3^{i}	1.480 (9)
N2—N1—C4	106.5 (5)	C5—N2—H2	116 (2)
N2—N1—H1	104 (2)	N1—C4—N3	117.1 (3)
C4—N1—H1	106 (2)	C4—N3—N3^{i}	103.7 (5)
N1—N2—C5	119.6 (4)	C4—N3—C5^{i}	107.7 (5)
N1—N2—H2	108 (3)	C5^{i}—N3—N3^{i}	109.8 (6)

Symmetry code: (i) $-x, -y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N2^{ii}	0.85 (4)	2.40 (4)	3.209 (9)	159 (3)
N2—H2···N3^{iii}	0.85 (2)	2.44 (3)	3.271 (8)	165 (3)

Symmetry codes: (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x, y-1, z$.

Data collection

Huber Guinier G670 diffractometer
Specimen mounting: pressed as a thin layer in the specimen holder
Specimen mounted in transmission mode
Scan method: step
Absorption correction: none
$2\theta_{min}$ = 3.0, $2\theta_{max}$ = 65.0°
Increment in 2θ = 0.01°

Refinement

Refinement on I_{net}
R_{wp} = 0.025
R_{exp} = 0.008
R_B = 0.019
S = 2.87
Wavelength of incident radiation: 1.54059 Å
Excluded region(s): 3.00–13.99
Profile function: split-type pseudo-Voigt
68 parameters
H atoms treated by a mixture of independent and constrained refinement
Weighting scheme based on measured s.u.'s; $w = 1/I_{obs}$
$(\Delta/\sigma)_{max}$ = 0.01
Preferred orientation correction: none

Monoclinic cell dimensions were determined with *TREOR90* (Werner *et al.*, 1985) using the first 53 peak positions. The structure was solved by the simulated annealing method and refined by Rietveld refinement using *MRIA* (Zlokazov & Chernyshev, 1992). The diffraction profile and the difference between the measured and calculated profiles after the final Rietveld refinement are shown in Fig. 3. This centrosymmetric small molecule has only five non-H atoms per asymmetric unit; this, as well as good diffraction data, allowed us to refine all non-H atoms isotropically without any bond length or U_{iso} restraints. H atoms bonded to N atoms were found in difference maps and their coordinates were refined independently, with U_{iso}(H) = 0.05 Å^2. H atoms bonded to C atoms were placed in geometrically calculated positions with U_{iso}(H) = 1.2U_{iso}(C). The specimen turned out to be texture-free.

Data collection: *HUBER G670* (HUBER Diffraktionstechnik GmbH, version 4.3); cell refinement: *MRIA* (Zlokazov & Chernyshev, 1992); data reduction: *HUBER G670*; program(s) used to solve

structure: *MRIA*; program(s) used to refine structure: *MRIA*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *MRIA*.

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References

Neureiter, N. P. (1959). *J. Am. Chem. Soc.* **81**, 2910.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Werner, P.-E., Eriksson, L. & Westdahl, M. (1985). *J. Appl. Cryst.* **18**, 367–370.
Zlokazov, V. B. & Chernyshev, V. V. (1992). *J. Appl. Cryst.* **25**, 447–451.