

1,6,7,12,13,18-Hexaazatrinaphthylene tetrachloroform solvate

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Key indicators

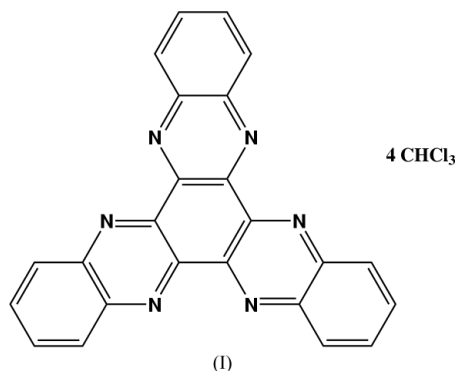
Single-crystal X-ray study
 $T = 223$ K
Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
 R factor = 0.036
 wR factor = 0.064
Data-to-parameter ratio = 15.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, 1,6,7,12,13,18-hexaazatrinaphthylene (HATN) tetrachloroform solvate, $\text{C}_{24}\text{H}_{12}\text{N}_6 \cdot 4\text{CH}_2\text{Cl}_2$, belongs to a series of planar bridging ligands with an extensive delocalized π -electron system. The planar molecules pack in pairs with a π - π stacking of a symmetry-related quinoline moiety and are surrounded by solvent molecules of chloroform. The latter are involved in $\text{C}-\text{H} \cdots \text{N}$ contacts with the six pyrazine N atoms.

Received 31 January 2001
Accepted 12 February 2001
Online 19 February 2001

Comment

Hexaazatrinaphthalene (HATN) is one of a series of compounds which contain three sites for possible bidentate coordination to a metal center. It is thought that delocalization of the π -electron system may provide facile electronic communication between coordinated metal centers leading to interesting physical properties. The parent compound of this series, 1,4,5,8,9,12-hexaazatriphenylene (HAT), has recently been reported to form a robust (10,3)-*a* network containing chiral micropores on coordinating Ag^{I} (Abrahams *et al.*, 1998). The chemistry of ruthenium(II) (Kirsch-De Mesmaeker *et al.*, 1989; Rutherford *et al.*, 1997) and mixed $\text{Ru}^{\text{II}}/\text{Os}^{\text{II}}$ (Rutherford & Keene, 1998) complexes of HAT have also been studied. The hexaphenyl derivative of HAT has been used to form a number of capped polymetallic complexes with copper(I) and silver(I) (Baxter *et al.*, 1999; Baxter, Lehn, Baum *et al.*, 1993; Baxter, Lehn, Kneisel *et al.*, 1999). The syntheses of a number of HAT derivatives have been reported (Rademacher *et al.*, 1994) and the crystal structure of HAT-hexacarboxamide was published in 1996 (Beeson *et al.*, 1996). The crystal structures



of a number of mono- and binuclear Pd^{II} and Re^{I} complexes with the hexamethyl derivative of HATN have been reported (Catalano *et al.*, 1994). Two trinuclear copper(I) complexes were recently synthesized (Okubo *et al.*, 1999) using the HAT-hexacarbonitrile anion, which was prepared electrolytically. The complexes were found to exhibit anion-trapping behavior in the solid state and in solution.

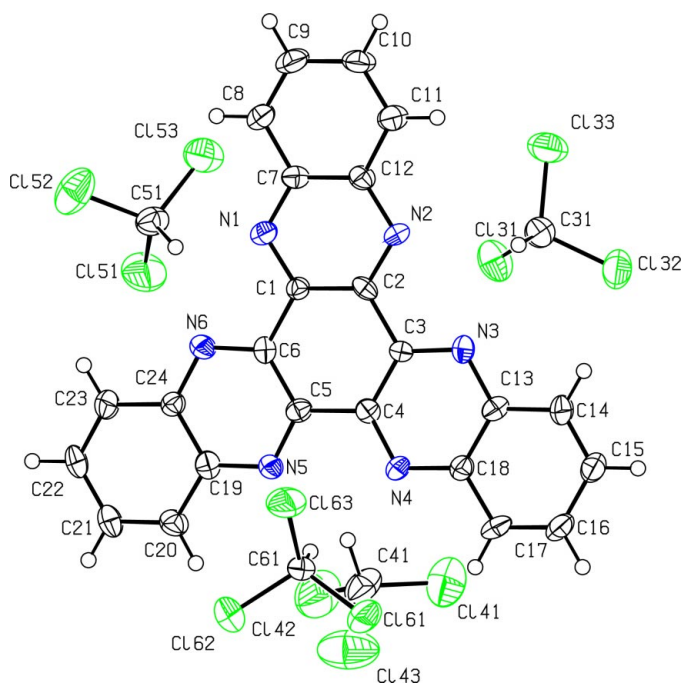


Figure 1
PLATON (Spek, 1990) plot of (I) (displacement ellipsoids at the 50% probability level).

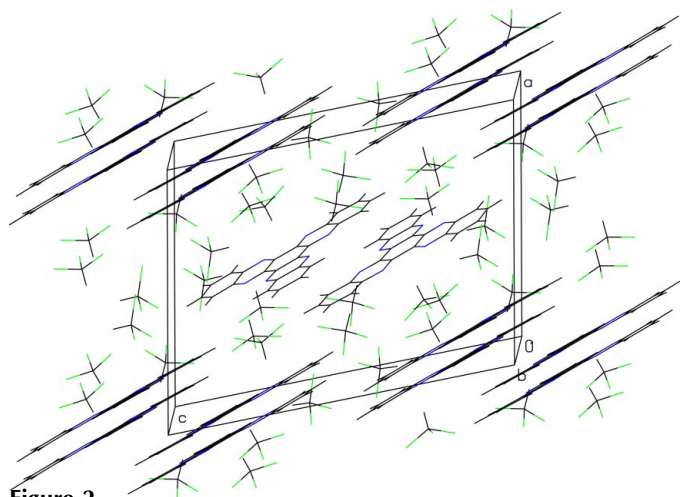


Figure 2
Packing diagram of the title compound viewed down the *b* axis, showing the CHCl_3 solvent molecules between pairs of HATN molecules and the $\text{C—H} \cdots \text{N}$ interactions.

The title compound, (I), crystallizes with four molecules of CHCl_3 per molecule of HATN. The molecule is planar with a maximum deviation for atom N3 of 0.034 Å from the least-squares plane through all of the non-H atoms comprising the molecule (Fig. 1). The pattern of bond distances and angles in HATN does not suggest a regular delocalized conjugated system as observed in HAT–hexacarboxamide (Beeson *et al.*, 1996). The central six-membered ring has three short fused bonds C1–C2, C3–C4 and C5–C6 [average value 1.425 (2) Å] and three long non-fused bonds C2–C3, C4–C5 and C6–C1 [average value 1.479 (2) Å]. The same pattern

was observed in HAT–hexacarboxamide (Beeson *et al.*, 1996) but with slightly shorter distances, *viz.* 1.405 (10) Å and 1.457 (6) Å, respectively. The remainder of the carbon–carbon bonds have an average value of 1.42 (1) Å except two bonds in the outer fused benzene rings. Surprisingly, here the average value is 1.351 (2) Å for bonds C8–C9, C10–C11, C14–C15, C16–C17, C20–C21 and C22–C23.

In the crystal the HATN molecules stack in pairs, related by a center of symmetry. These ‘dimers’ stack up the *a* axis and are surrounded by solvent molecules of chloroform (Fig. 2). Each pyrazine N atom is involved in a $\text{C—H} \cdots \text{N}$ contact with the chloroform solvent molecules. Details are given in Table 2. The symmetry-related quinoline moieties involving atoms N1/N2/C1/C7–C12/C2 [symmetry code: $1 - x, 1 - y, 1 - z$], are overlapped with an average non-bonded interatomic distance of 3.66 (1) Å. This is larger than the expected van der Waals separation of *ca* 3.2 Å for π -complexation of aromatic rings. In contrast, it was found that molecules of HAT–hexacarboxamide (Beeson *et al.*, 1996) also stack in pairs but with an average separation of 3.31 (9) Å, indicating the presence of π -complexation.

Experimental

Hexaketocyclohexane octahydrate (1.0 g, 3.20 mmol) and 1,2-phenylenediamine (1.14 g, 10.5 mmol) were added to 200 ml of absolute ethanol. The reaction mixture was refluxed for 12 h after which the solution was cooled to room temperature. The pale-orange precipitate was filtered off and dried under vacuum. Recrystallization from CHCl_3 gave extremely thin orange plate-like crystals.

Crystal data

$\text{C}_{24}\text{H}_{12}\text{N}_6 \cdot 4\text{CH}_3\text{Cl}$
 $M_r = 861.87$
 Monoclinic, P_1/n
 $a = 15.1170$ (13) Å
 $b = 11.6285$ (6) Å
 $c = 19.9737$ (16) Å
 $\beta = 101.624$ (10)°
 $V = 3439.1$ (4) Å³
 $Z = 4$

$D_x = 1.665$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4774 reflections
 $\theta = 2.0$ – 25.9°
 $\mu = 1.00$ mm⁻¹
 $T = 223$ (2) K
 Plate, orange
 $0.35 \times 0.15 \times 0.10$ mm

Data collection

Stoe IPDS diffractometer
 φ oscillation scans
 26 548 measured reflections
 6626 independent reflections
 1836 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.168$
 $\theta_{\text{max}} = 25.9^\circ$
 $h = -18 \rightarrow 18$
 $k = -14 \rightarrow 13$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.064$
 $S = 0.57$
 6626 reflections
 431 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0002P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³

Table 1
Selected geometric parameters (Å).

N1—C1	1.332 (5)	C7—C8	1.423 (6)
N1—C7	1.355 (6)	C7—C12	1.414 (6)
N2—C2	1.318 (5)	C9—C10	1.410 (7)
N2—C12	1.364 (5)	C10—C11	1.352 (6)
N3—C3	1.319 (6)	C11—C12	1.409 (6)
N3—C13	1.382 (5)	C13—C14	1.409 (6)
N4—C4	1.325 (5)	C13—C18	1.422 (6)
N4—C18	1.360 (6)	C14—C15	1.347 (6)
N5—C5	1.327 (6)	C15—C16	1.426 (7)
N5—C19	1.348 (6)	C16—C17	1.350 (7)
N6—C6	1.327 (6)	C17—C18	1.415 (6)
N6—C24	1.352 (6)	C19—C20	1.412 (7)
C1—C2	1.423 (6)	C19—C24	1.437 (5)
C1—C6	1.472 (6)	C20—C21	1.352 (7)
C2—C3	1.491 (6)	C21—C22	1.405 (6)
C3—C4	1.428 (6)	C22—C23	1.351 (7)
C4—C5	1.475 (6)	C23—C24	1.410 (6)
C5—C6	1.425 (6)		

Table 2
Hydrogen-bonding 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>
C31—H31...N2	0.87 (4)	2.60 (4)	3.260 (7)	134 (4)
C31—H31...N3	0.87 (4)	2.57 (5)	3.268 (7)	138 (4)
C41—H41...N5	1.06 (5)	2.51 (5)	3.493 (6)	154 (4)
C51—H51...N1	1.17 (4)	2.50 (4)	3.489 (6)	141 (3)
C51—H51...N6	1.17 (4)	2.37 (4)	3.415 (6)	147 (3)
C61—H61...N4	0.96 (4)	2.62 (5)	3.332 (7)	132 (4)
C61—H61...N5	0.96 (4)	2.53 (5)	3.333 (7)	141 (4)

The R_{int} value is rather high, which is probably due to the poor quality of the crystal and its small thickness. Less than one third of the unique reflections can be considered to be observed and the ratio of observed reflections to parameters is only 4.3. The aromatic H atoms were placed in calculated positions and treated as riding atoms using

SHELXL97 default parameters. The CHCl_3 H atoms were located from Fourier difference maps and refined isotropically.

Data collection: *EXPOSE* (Stoe, 2000); cell refinement: *CELL* (Stoe, 2000); data reduction: *INTEGRATE* (Stoe, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON99* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

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

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