

Unexpected conformational consequences of weak hydrogen bonds on 1,3,7,9,13,15,19,21-octaazapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane monohydrate

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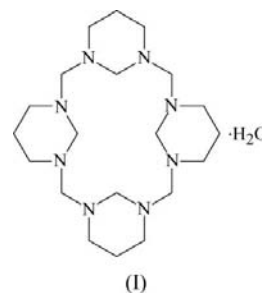
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In the title compound, C₂₀H₄₀N₈·H₂O, the organic molecule crystallizes with one water molecule located within the molecular cavity of the octaaza macrocycle. The two molecules are linked *via* two weak O—H...N hydrogen bonds. The assembly has noncrystallographic C₂ axial symmetry.

Comment

Polyaza macrocyclic compounds with tetrahedrally arranged nitrogen lone-pair orbitals (LPOs) have been exploited for complexation with ions (Mazloum *et al.*, 2002). Some of these compounds have attracted intense attention due to their molecular diamond lattice conformation. In fact, both theoretical (Galasso *et al.*, 2001) and experimental studies (Dale *et al.*, 1991, 1992) of the molecular structures and spectroscopic properties of this class of compounds have been reported. The results of these studies revealed that 1,3,7,9,13,15,19,21-octaazapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane exists in two conformations, one in which the eight N atoms are diequatorially substituted (*D*_{2d} symmetry) and one with an equatorial–axial substitution in each 1,3-diazane ring (*S*₄ symmetry). Density functional theory (DFT) calculations (Galasso *et al.*, 2001) showed that the *S*₄ conformer is more stable than the *D*_{2d} conformer by 2.6 kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ mol⁻¹), due to dipole–dipole repulsion between the axial lone pairs of the N atoms. A previous X-ray structural investigation of a 1:1 complex of 1,3,7,9,13,15,19,21-octaazapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane and benzene showed that the 16-membered pentacyclooctaaza ring exists in a less symmetric but more stable conformation (Murray-Rust, 1975). However, the most favourable conformation is avoided when 1,3,7,9,13,15,19,21-

octaazapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane crystallizes as a 1:2 dichloromethane complex (Dale *et al.*, 1991), where the *D*_{2d} conformation exhibits a *syn*-axial orientation of the N-atom lone pairs, showing the so-called rabbit-ear effect (Hutchins *et al.*, 1968). Repulsion is avoided due to the presence of intermolecular interactions between the N atoms and the H atoms of the dichloromethane molecules (Dale *et al.*, 1991).



In recent years, we have used these classes of polycyclic polyaza compounds, as preformed Mannich reagents, in the synthesis of several heterocyclic systems (Rivera *et al.*, 2005; Rivera & Maldonado, 2006). During these studies, crystals of the title monohydrate, (I), were obtained when the reaction was carried out according to the usual technique, *i.e.* mixed aqueous formaldehyde and propane-1,3-diamine (Krassig, 1956). A broad band with a maximum at about 3400 cm⁻¹ is observed in the IR spectrum, which is attributed to water molecules. Although selective inclusion of nonprotic solvents such as benzene, dioxane and dichloromethane by 1,3,7,9,13,15,19,21-octaazapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane is known (Dale *et al.*, 1991), where host–guest association determines the conformational preference of the organic molecule, as far as we are aware this is the first example of a complex of this macrocycle with a protic solvent. The current X-ray crystal structure analysis confirms that this

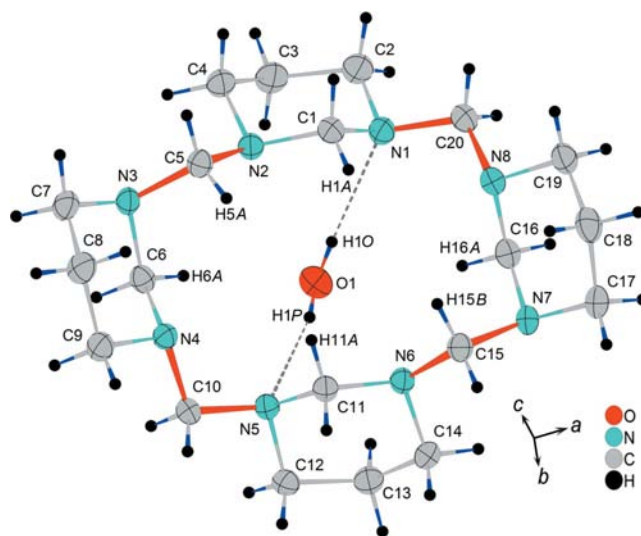


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

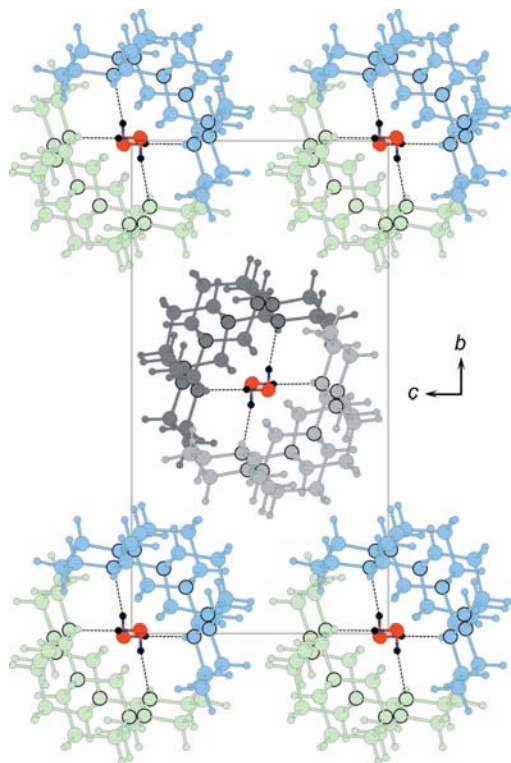


Figure 2
The packing of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds.

solid is a 1:1 complex of the 1,3,7,9,13,15,19,21-octaaza-pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane macrocycle and a water molecule. Only two of the eight N atoms of the macrocycle are involved in hydrogen bonding with the molecule of water. Our results indicate that the title macrocycle affords efficient binding affinity for both apolar and polar solvents due to the chelation effect, and could thus form complexes with metallic cations (Mazloum *et al.*, 2002).

The molecular structure and atom-numbering scheme for (I) are shown in Fig. 1. All atoms of both the organic molecule and the water molecule are located on general positions. Selected angles and bond lengths are listed in Table 1. Careful examination of the crystal structure of the adduct shows that the 1,3-diazane rings adopt two different conformations, which are only controlled by the binding of the water molecule. One of the conformations is hydrogen bonded and the other is not (Fig. 1). Our crystal structure analysis results show that the hydrogen-bond interactions in (I) do not generate a large change in the tetrahedral character of the N-atom lone pairs. The marked tetrahedral character of the N atoms in (I) is nicely illustrated by the sums of the C–N–C bond angles, which range from 330.2 to 336.4°. The individual C–N–C bond angles in (I) are around 109.2 (1)–113.8 (1)° (Table 1), close to normal tetrahedral bond angles. Nevertheless, as can be seen in Table 1, the smallest values are for the N atoms involved in hydrogen bonding (N1 and N5). This crystal structure analysis also shows that the aminal C–N bond lengths for N atoms neighbouring N atoms involved in hydrogen-bond interactions are shorter than the other bonds.

The presence of hydrogen bonds to atoms N1 and N5 might enhance the structural consequences, and thus the formation of this class of intermolecular interactions strongly influences the conformation of the molecule, forming the less stable configuration with a 1,3-diaxial disposition of the nitrogen lone pairs and forcing the hexahydropyrimidine ring to adopt a diequatorial disubstitution. This can be explained on the basis of a preference for the conformation where the lone pair is located in the proximity of the electrostatic dipole–dipole interaction, the so-called reverse anomeric effect (Grein & Deslongchamps, 1992). On the other hand, for the other two rings, the stable conformation is conserved. The ring structure is approximately C_2 symmetric with a twofold axis passing through atom O1. On the basis of our results, we propose the existence of a third conformation for the organic molecule of (I).

Fig. 2 shows the crystal packing in (I), with the channels extending along the *a* axis and accommodating the water molecules. Each channel is composed of two symmetry-equivalent positions of the organic molecule. No remarkable intermolecular contacts exist in the structure.

Experimental

To a stirred solution of formaldehyde (16.4 ml, 0.22 mmol, 40% in ethanol), propane-1,3-diamine (8 ml, 0.11 mmol) and a solution of NaOH (0.25 M; 0.1 ml, 0.02 mmol) were added dropwise slowly. After stirring for 12 h at room temperature, the solvent was removed at reduced pressure. Recrystallization of the resulting solid from ethanol–water (80:20 *v/v*) gave diffraction quality crystals of the title compound, (I) (m.p. 438–439 K).

Crystal data

$C_{20}H_{40}N_8 \cdot H_2O$	$V = 2293.58 (7) \text{ \AA}^3$
$M_r = 410.6$	$Z = 4$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation
$a = 12.4858 (2) \text{ \AA}$	$\mu = 0.61 \text{ mm}^{-1}$
$b = 18.8016 (3) \text{ \AA}$	$T = 120 \text{ K}$
$c = 9.8354 (2) \text{ \AA}$	$0.43 \times 0.37 \times 0.26 \text{ mm}$
$\beta = 96.6010 (13)^\circ$	

Data collection

Oxford Xcalibur diffractometer	43976 measured reflections
with an Atlas detector (Gemini Ultra Cu)	4010 independent reflections
Absorption correction: multi-scan (CrysAlis Pro; Oxford Diffraction, 2009)	3741 reflections with $I > 3\sigma(I)$
$T_{\min} = 0.716$, $T_{\max} = 1.000$	$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.125$	
$S = 2.73$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
4010 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
268 parameters	

All H atoms were discernible in difference Fourier maps and could be refined to a reasonable geometry. According to common practice, H atoms attached to C atoms were nevertheless kept in ideal positions during the refinement, with C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The water H atoms were refined isotropically.

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.4630 (13)	N5—C10	1.4606 (13)
N1—C2	1.4739 (14)	N5—C11	1.4673 (14)
N1—C20	1.4663 (15)	N5—C12	1.4697 (13)
N2—C1	1.4448 (14)	N6—C11	1.4443 (13)
N2—C4	1.4611 (14)	N6—C14	1.4611 (13)
N2—C5	1.4524 (13)	N6—C15	1.4499 (14)
N3—C5	1.4596 (13)	N7—C15	1.4574 (13)
N3—C6	1.4558 (13)	N7—C16	1.4484 (14)
N3—C7	1.4659 (14)	N7—C17	1.4665 (15)
N4—C6	1.4724 (13)	N8—C16	1.4761 (14)
N4—C9	1.4613 (13)	N8—C19	1.4631 (15)
N4—C10	1.4526 (14)		
C1—N1—C2	110.30 (9)	C10—N5—C11	110.07 (8)
C1—N1—C20	110.48 (9)	C10—N5—C12	109.20 (8)
C2—N1—C20	109.39 (8)	C11—N5—C12	110.11 (8)
C1—N2—C4	110.42 (8)	C11—N6—C14	110.63 (8)
C1—N2—C5	112.89 (8)	C11—N6—C15	112.88 (8)
C4—N2—C5	112.94 (8)	C14—N6—C15	112.85 (8)
C5—N3—C6	112.24 (8)	C15—N7—C16	112.24 (8)
C5—N3—C7	113.41 (8)	C15—N7—C17	113.75 (8)
C6—N3—C7	109.85 (8)	C16—N7—C17	110.15 (8)
C6—N4—C9	109.71 (8)	C16—N8—C19	109.39 (9)
C6—N4—C10	111.36 (8)	C16—N8—C20	110.79 (9)
C9—N4—C10	111.40 (8)	C19—N8—C20	111.70 (8)

Table 2

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>
O1—H1O···N1	0.886 (16)	2.248 (16)	3.1226 (12)	169.3 (12)
O1—H1P···N5	0.890 (16)	2.226 (15)	3.1008 (12)	167.4 (15)

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure:

JANA2006 (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3369). Services for accessing these data are described at the back of the journal.

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