1,3,7,9,11,15,17,19,23,25,27,34-Dodecaazanonacyclo-[25.5.3.$2^{6,9}$.$2^{14,17}$.$2^{22,25}$.$1^{3,7}$.$1^{11,15}$.$1^{19,23}$.$0^{30,34}$]-tetratetracontane

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Pentane-1,3,5-triamine condenses with formaldehyde to give directly and exclusively the nonacyclic title compound, whose conformations have been studied by X-ray analysis and low-temperature ^{13}C NMR spectroscopy.

In 1955 Krässig observed that propane-1,3-diamine undergoes a remarkably easy condensation with formaldehyde to give the quinquecyclic compound **1** having a central 16-membered ring laterally fused with four 6-membered rings.[1] It can exist in two diamond-lattice conformations and both have been observed.[2,3] We have since enlarged the scope of this fascinating example of self assembly.[4,5]

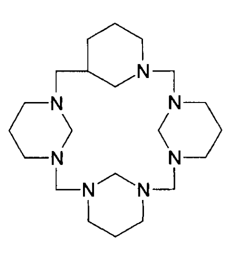
The conclusion that it is the conformational adherence to the diamond-lattice geometry of these ring systems that explains their ease of formation and their stability, led to the prediction that pentane-1,3,5-triamine should condense similarly with formaldehyde to give the nonacyclic product **2** having a central 24-membered ring laterally fused with four *trans*-decalin-like units.

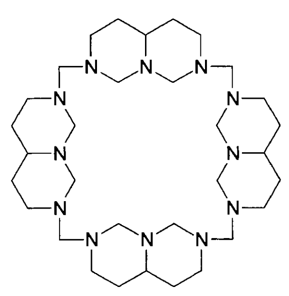
Pentane-1,3,5-triamine was synthesized according to Rüssel[6] and carefully purified by distillation. To a solution of this triamine in water at 10 °C was added dropwise an aqueous solution of formaldehyde (molar ratio of reactants 1 : 3). After *ca* 30 min, compound **2** precipitated in 100% yield, mp 221 °C; ^{13}C NMR ([^{2}H$_8$]toluene): δ 73.6, 71.9, 62.6, 50.0, 30.1. MS (EI): 613 (M + 1), 459, 307, 305, 153. Compound **2** is soluble in most organic solvents.

Whereas **1** can choose between only two diamond-lattice conformations, of symmetry D_{2d} and S_4, respectively,[2,3] compound **2** has four possibilities. These are shown in Fig. 1 with symmetries indicated, but are more precisely defined by the number and sequence of 'axial' *a* and 'equatorial' *e* attachments of the links between the four *trans*-decalin-like moieties: **A** = *ee*, *ee*, *ee*, *ee* (five ^{13}C lines at slow exchange); **B** = *ea*, *ea*, *ea*, *ea* (eight lines); **C** = *ea*, *ae*, *ea*, *ae* (nine lines); **D** = *aa*, *aa*, *aa*, *aa* (five lines).

The relatively large cavity of conformations **A** and **B** suggests that molecular complexes or clathrates might be formed. Compound **2** does indeed crystallize as various solvates. A satisfactory X-ray structure determination was achieved for the tetrahydrate, as crystallized from moist ethyl acetate, and is shown in Fig. 2.† It reveals the perfect conformation **A**, which is not surprising, considering that it is all-equatorial (*cf.* the strong equatorial preference for the methyl group in *N*-methylpiperidine[7]). The four water molecules were found to be distributed over 12 sites, all at reasonable hydrogen-bond distances from nitrogen atoms.

In solution the situation is more complex. At room temperature the ^{13}C NMR spectrum in any solvent shows five lines of relative intensities 1 : 2 : 1 : 2 : 2 corresponding to the chemical symmetry. Since carbon site-exchange is rapid, this can represent any time-averaged mixture of conformers. On cooling, the lines broaden and then split in the range −20 to −50 °C. At −110 °C in CD$_2$Cl$_2$–CHCl$_2$F the resolved spectrum appears as shown in Fig. 3. Our interpretation is that the conformer


1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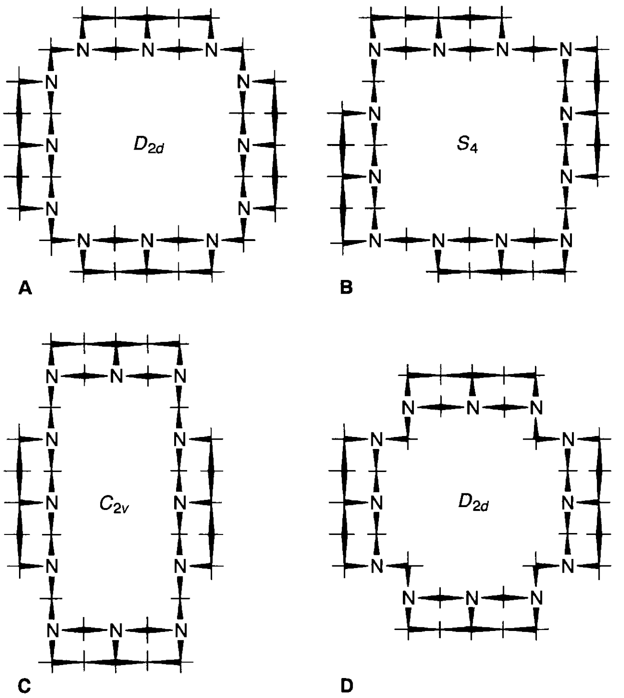

Fig. 1 Bird's-eye view of the four possible diamond-lattice conformations of **2**

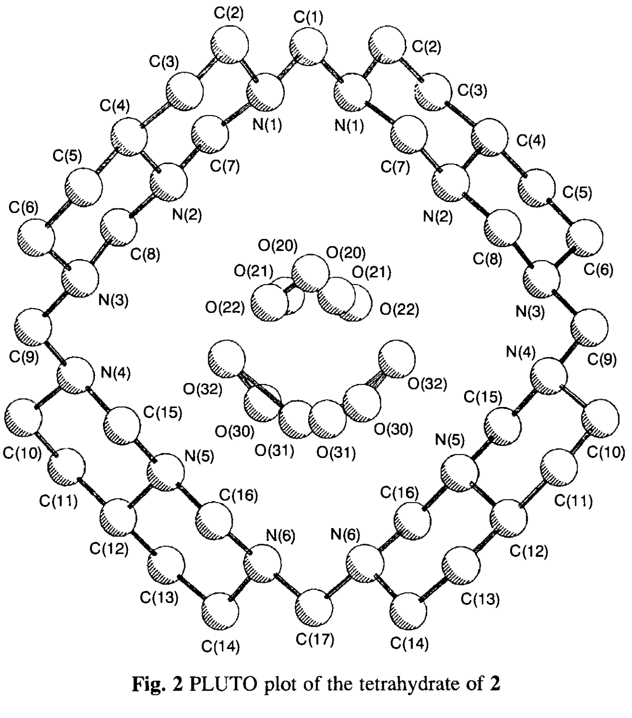

Fig. 2 PLUTO plot of the tetrahydrate of **2**

mixture is dominated by roughly equal quantities of **B** and **C**. This requires 17 lines, so that among the 15 resolved strong lines, those two which are particularly strong must represent two each. All dominating lines are then correctly grouped in the four chemical shift regions. The presence of a minor third conformer assigned to **A** is betrayed by weak lines near δ 30 and 60, marked **A** in Fig. 3, but the remaining three lines are not sufficiently resolved. In CD_2Cl_2–[$^2H_5$]pyridine the situation is reversed; conformer **A** (five lines) dominates over equal quantities of **B** and **C**.

No indication was found of transannular bridge-complexation of **2** with CH_2Cl_2, as was observed[3] for **1**. A short HCH bridge would only be possible for the 'rectangular' **C**, and not for the 'square' **B**.

A multistep interconversion mechanism is postulated for the observed low-barrier carbon-site exchange. Unpopulated intermediate conformers are needed, and each step would consist of a slow nitrogen inversion followed by fast adjustments of torsion angles in the CN bonds connecting the rigid 'decalin' units. Since the transition from fast to slow exchange takes place in the same temperature range (−20 to −50 °C) to reveal simultaneously all populated species, we conclude that the barriers in all inversion steps have roughly the same height of about 45 kJ mol^{-1}. This is close to the barrier observed[3] for **1** and supports the view that only the linkages between the lateral ring units are involved.

A second process, the high-barrier site-exchange of geminal hydrogens could be observed in the ^1H NMR spectrum of **1** on heating to about 100 °C in [$^2H_8$]toluene (T_c *ca.* 30–60 °C).[3] It involves all CH_2 groups (although not observable for the symmetrical CH_2 groups connecting the lateral units). Such a process is not possible for **2** since it requires that inversion can take place at all bridgeheads. In **1** all eight bridgeheads are nitrogen atoms, whereas four of the 16 bridgeheads in **2** are CH groups that will block the process. In fact, no change in the ^1H NMR spectrum could be seen on heating a [$^2H_8$]toluene solution from room temperature to > 100 °C.

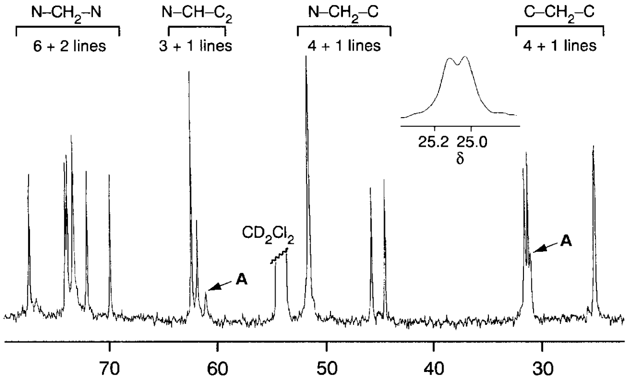

Fig. 3 125 MHz ^{13}C NMR spectrum of **2** in CD_2Cl_2–$CHCl_2F$ at −110 °C. The expected number of lines in the four chemical shift regions for a mixture of **A**, **B** and **C** are given.

This led to the prediction that a compound analogous to **2**, having nitrogen at all 16 bridgeheads, should permit geminal exchange. Its synthesis and properties are the subjects of the following communication.[8]

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Footnote

† *Crystal data* for **2**: $C_{32}H_{60}N_{12}\cdot 4H_2O$, colourless crystals, orthorhombic, space group *Pbcn*, a = 13.886(1), b = 21.587(3), c = 12.798(1) Å, V = 3836.4(7) Å^3, Z = 4, T = 293 K, crystal dimensions 0.20 × 0.25 × 0.25 mm, 3800 reflections measured, range ($3 < 2\theta < 52°$), 1728 observed with $I > 3\sigma(I)$, μ = 0.8 cm^{-1}; final R = 0.040 and Rw = 0.043 (395 parameters, $w = 1/\sigma^2 (F_c{}^2)$; maximum shift/error = 0.19; ρ_{max} = 0.11 e Å^{-3}, ρ_{min} = −0.17 e Å^{-3}; X-ray experimental procedures: Mo-Kα radiation (λ = 0.71069 Å), graphite crystal monochromator, Enraf-Nonius CAD4 diffractometer (ω–2θ scan technique). The structure was determined by direct methods (MITHRIL) and anisotropically refined (NRCVAX), drawing made using PLUTO. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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