

1,7,13,19-Tetramethyl-3,5,9,11,15,17,21,23-octaazasepticyclo-[11.11.5.5^{7,19,13,23,15,9,11,15,17,21}]octatriacontane

Johannes Dale, Christian Rømming and M. Rachel Suissa

Kjemisk Institutt, Universitetet i Oslo, 0315 Oslo, Norway

2,8-Dimethyl-2,8-bis(aminomethyl)nonane-1,9-diamine, prepared by catalytic hydrogenation of 2,2,8,8-tetracyanononane, condenses with formaldehyde to precipitate a polymer which by heating is isomerized to the septicyclic title compound, whose X-ray structure has been determined.

The condensation of ammonia with formaldehyde to give 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane of adamantane-like structure is perhaps the earliest known example¹ of the formation of a multicyclic compound by self-assembly. In 1955 Krässig² reported an equally facile condensation of propane-1,3-diamine with formaldehyde to give 1,3,7,9,13,15,19,21-octaazaquinquecyclo[19.3.1.1^{3,7,19,13,15,19}]octacosane. Recently, we have demonstrated its existence in solution in two diamond-lattice conformations of S_4 and D_{2d} symmetry,³ the former crystallizing as a clathrate with benzene,⁴ the latter as a 1:2 complex with dichloromethane.³ Subsequently, we found that also 2,2-dimethylpropane-1,3-diamine reacts with formaldehyde to give, with the same remarkable ease, the octamethyl-substituted quinquencyclic compound.⁵ It crystallizes without solvent in the D_{2d} conformation **1**, which is also the exclusive conformation in solution.⁵

As shown in structure **2**, it would seem possible to complete

the diamond lattice by replacement of the four inner methyl groups with two pentamethylene bridges, one above and the other below the central 16-membered ring, to give a compact molecule with the external shape of a tetrahedron. The close interaction of internally directed CH_2 groups with the aminal lone pairs was not considered prohibitive in view of the evidence for an analogous and permitted interaction of an axial 5-*tert*-butyl group with the oxygen lone pairs of 1,3-dioxanes.⁶

The synthesis of this molecule has now been achieved. Monomethylmalonodinitrile and 1,5-dibromopentane gave 2,2,8,8-tetracyanononane (m.p. 96 °C, 92%), which on catalytic hydrogenation (W2-Raney nickel, NH_3 satd. ethanol, 90 atm, 90 °C) yielded 2,8-bis(aminomethyl)-2,8-dimethylnonane-1,9-diamine (m.p. 113–115 °C, 90%). To a cooled aqueous solution of this tetramine was dropped rapidly a formalin solution in excess, causing immediate precipitation of a polymer, insoluble in all organic solvents. However, in refluxing dioxane overnight the polymer gradually dissolved, and, after concentration and cooling, a crystalline compound was obtained (m.p. 239–240 °C, 81%). It was slightly soluble in most organic solvents, and showed ^1H and ^{13}C spectra in accord with the structure **1** of the title compound. It is of interest that the four strongest peaks above m/z 100 in the mass spectrum (EI, 70 eV) came at 584 (M^+), 293 ($M/2 + 1^+$), 292 ($M/2^+$) and 291 ($M/2 - 1^+$), which means that the molecule has fragmented into just two halves. This suggests a concerted rupture of eight CN bonds, resulting in the total destruction of the central 16-membered ring and the opening of all four 6-membered rings.

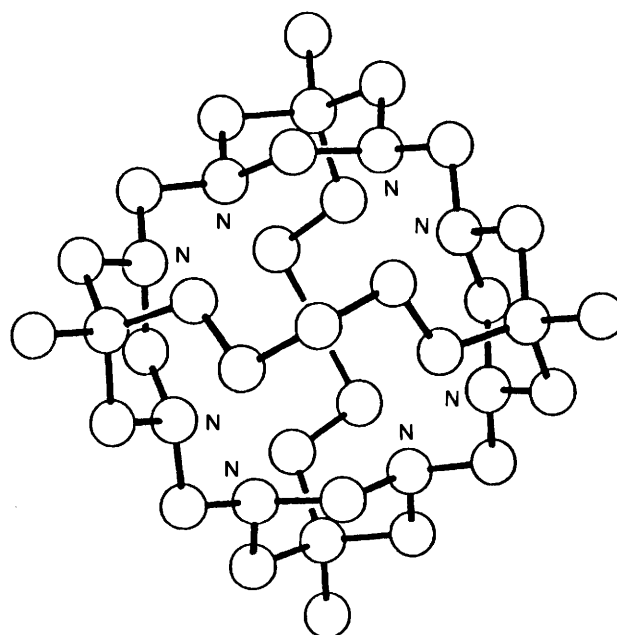
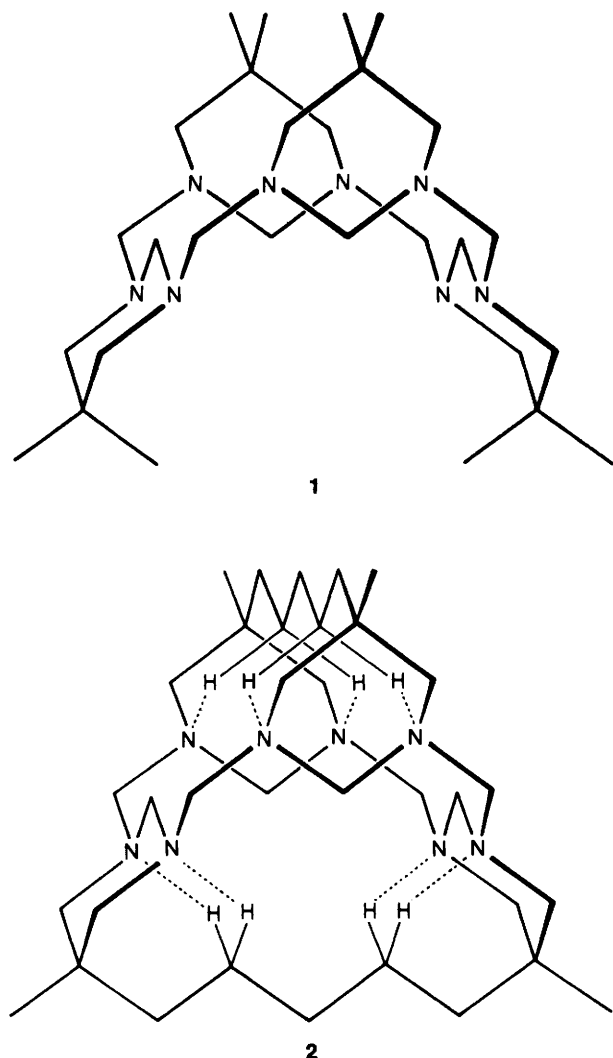


Fig. 1 PLUTO plot of the molecule as seen down the fourfold inversion axis

Much to our surprise, the X-ray analysis[†] of the crystal structure (Fig. 1) revealed that the conformation of each of the two pentamethylene bridges is not that of the extended all-*anti* chain, but has a sequence of $g^\pm, a, g^\mp, g^\mp, a, g^\pm$ torsion angles. Clearly, the close interaction of the nitrogens with the β -methylene groups of the extended chain is in this case repulsive. The observed S_4 symmetric structure implies the presence of some strain due to the departure from the ideal torsion angles of 60 and 180° attainable only in the expected D_{2d} conformation. The X-ray analysis shows that this strain is evenly distributed over the whole molecular skeleton by allowing moderate deviations in practically all bonds, *gauche* angles ranging from 56 to 73° and *anti* angles from 158 to 179°.

[†] *Crystal data:* C₃₄N₈H₆₄, colourless crystals, tetragonal, space group $P4_1/a$, $a = 15.035(3)$, $c = 15.207(3)$ Å, $V = 3437.6(1.1)$ Å³, $Z = 4$, $D_c = 1.130$ g cm⁻³, $T = 138$ K, crystal dimensions 0.20 × 0.25 × 0.25 mm³, 1581 reflections measured, range ($3 < 2\theta < 50^\circ$), 801 observed with $I > 3\sigma(I)$, $\mu = 0.59$ cm⁻¹. Final $R = 0.039$ and $R_w = 0.033$ (160 parameters, $w = 1/[\sigma^2(F_o^2) + 0.0002F_o^2]$; maximum shift/error = 0.06, $\rho_{\max} = 0.17$ e Å⁻³, $\rho_{\min} = -0.15$ e Å⁻³. X-Ray experimental procedures: Mo-K α radiation ($\lambda = 0.71069$ Å), graphite crystal monochromator, Nicolet P3/F single crystal diffractometer (ω - 2θ scan technique). Semiempirical absorption correction was applied. The structure was determined by direct methods (MITHRIL) and anisotropically refined (GX Package), drawing made using PLUTO. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The observed initial precipitation of an insoluble aminal-type polymer and its subsequent isomerization to the soluble cage molecule is reminiscent of the reported condensation of glycoluril with formaldehyde to give first an insoluble polymer which is then isomerized, by acid, to the cage-like cucurbit[6]uril.⁷ Also a related cage compound, decamethylcucurbit[5]uril, has recently been prepared.⁸

The scope of the present self-assembly reaction is being further investigated by the use of tetraamines having shorter and longer connecting chains.

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