263. Correct Structure of a Condensation Product $C_6H_{12}N_4O_4$ from Hydrazine, Formaldehyde and Hydrogen Peroxide

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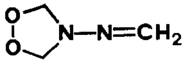
Summary

The compound mentioned in the title is shown by X-ray analysis to be 1,2,7,8-tetraaza-4,5,10,11-tetraoxatricyclo[6.4.1.1^{2,7}]tetradecane, contrary to previous suggestions. The torsion angle about the peroxo bonds in the seven-membered rings in 100°, close to the value in hydrogen peroxide, which would not be possible in a six-membered ring.

The colourless crystalline compound obtained by the reaction of hydrazine with formaldehyde in the presence of hydrogen peroxide [1] was first assigned an incorrect monocyclic structure **1**. The compound was later shown to have the double molecular weight and was assigned the tricyclic structure **2** mainly from its IR. and UV. spectra [2]. More recently, the conformational equilibrium of the compound has been discussed [3] on the basis of the ^{13}C- and ^{1}H-(300 MHz)NMR. spectra measured at temperatures down to 200 K. Our attention was directed to **2** as a possible candidate for a low-temperature X-ray crystallographic study aimed at the characterization of the bonding electron density in polar and nonpolar bonds [4].



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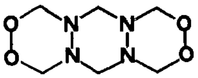

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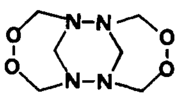

3

The results of a low-temperature (96 K) X-ray analysis leave no doubt that the structure is not **2** but **3**. A stereo-view of the centrosymmetric molecule is shown in *Figure 1*, bond lengths and angles in *Figure 2*. The identity of our compound with that studied by *Katritzsky et al.* [3] is established by the similarity of measured with published NMR. spectra, which appear to be just as compatible with structure **3** as with **2**, or even better, since at low-enough temperature one would expect the high-resolution ^{1}H-NMR. spectrum of **3** to consist of three *AB*-systems, which is what is observed [3].

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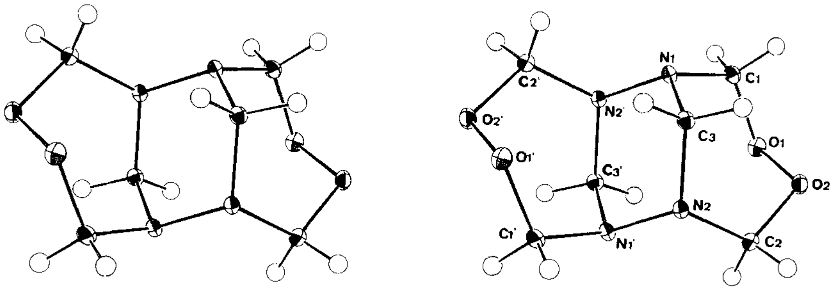

Fig. 1. *Stereo-view of* **3** *prepared by program ORTEP* [9] (Vibration ellipsoids are shown at the 50% probability level)

Since the reaction leading to **3** is reversible, structure **3** should be thermodynamically more stable than **2**, although it contains the two seven-membered rings whose existence was discounted in the arguments leading to the incorrect structure [2]. The tetraaza-cyclohexane ring has the chair conformation with all four N-lone pairs pointing in equatorial directions. The exocyclic N(1),C(1)-bond is

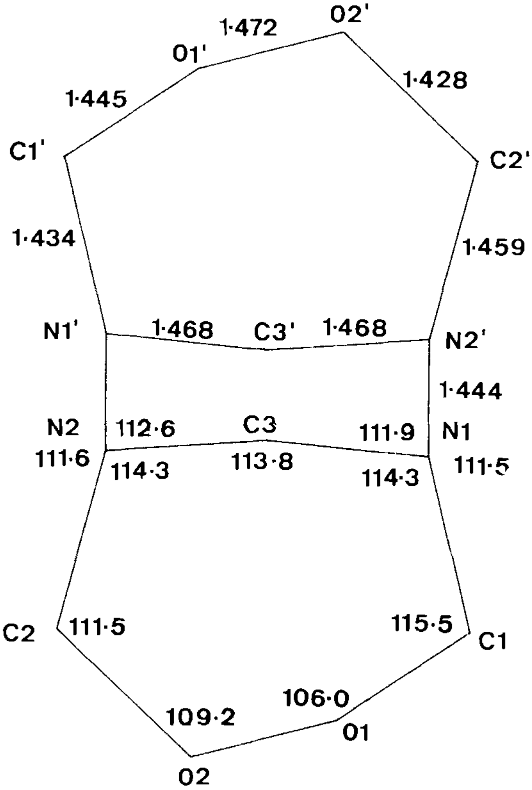

Fig. 2. *Bond distances (Å) and angles (deg.) in the centrosymmetric molecule* **3** (Standard deviations are about 0.001 Å and 0.1°)

0.025(2) Å shorter than N(2),C(2), while C(1),O(1) is 0.017(2) Å longer than C(2),O(2), differences that clearly depend on stereoelectronic factors, the lone pair at N(1) being antiperiplanar to the C(1),O(1)-bond while the lone pair at N(2) is anticlinal to C(2),O(2). In the seven-membered ring the torsion angle about the O,O-bond is 100°, close to the equilibrium torsion angle of about 112° in hydrogen peroxide [5]. In a six-membered ring with approximately tetrahedral bond angles it is almost impossible to obtain a torsion angle much greater than 60°, and this restriction may be the main reason for the thermodynamic stability of **3** compared with **2** since the energy penalty for deviating so far from the equilibrium conformation would be 10 kJ mol^{-1} or more per O,O-bond, the barrier at the syn-planar conformation being about 30 kJ mol^{-1} [5]. This argument implies that seven-membered peroxides should generally be more stable than their better known, six-membered counterparts, a generalization that might provoke an experimental enquiry into the matter.

Crystal Structure of 1,2,7,8-tetraaza-4,5,10,11-tetraoxatricyclo[6.4.1.1^{2,7}]tetradecane (3). - $C_6H_{12}N_4O_4$, M = 204.18. Crystals are triclinic, space group $P\bar{1}$, $Z = 1$ with cell dimensions $a = 6.065(3)$, $b = 6.136(1)$, $c = 6.574(1)$ Å, $\alpha = 105.99(1)$, $\beta = 102.52(2)$, $\gamma = 112.77(3)°$ at 96 K (6.123, 6.194, 6.645 Å, 105.82, 102.92, 112.67° at room temperature). Intensity measurements were made at 96 K with an *Enraf-Nonius* CAD4-diffractometer equipped with graphite monochromator (MoKα, $\lambda = 0.7107$ Å) and cooling device. 1773 independent reflexions were measured, 1413 with $I > 5\sigma$ (I). The structure was solved by direct methods using the program-system SHELX [6] and refined by full-matrix least-squares analysis using SHELX and XRAY 72 [7] programs with a modified weighting scheme with $r = 4.0$ Å^2 [8] and an extinction correction. The final R factor was 0.027, R_W was 0.033.

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