The Structure of the Ethylenediamine–Formaldehyde Condensation Product

By F. G. RIDDELL* and P. MURRAY-RUST
(*Chemistry Department, University of Stirling, Stirling, Scotland*)

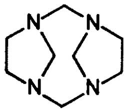
Summary The structure of the principal condensation product between ethylenediamine and formaldehyde is not 1,3,6,8-tetra-azatricyclo[6,2,1,$1^{3,6}$]dodecane (I) but is 1,3,6,8-tetra-azatricyclo[4,4,1,$1^{3,8}$]dodecane (II), the molecules of which show an interesting inversion process both in the solid and in solution.

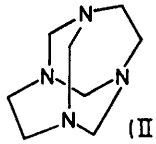
THE principal product (m.p. 196°) of the condensation reaction between ethylenediamine and formaldehyde in alkaline conditions was assigned the structure (I) by Bischoff in 1898.[1,2] Subsequent workers[3,4] saw no reason to doubt this structure which has now passed into general acceptance.[5] We have, however, accumulated evidence which unequivocally supports structure (II) for this compound rather than (I).

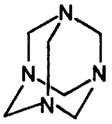
The n.m.r. spectrum of the compound was obtained in a variety of solvents. In all cases two relatively sharp singlets were observed at τ 6·0—6·2 and 6·8—7·1. This evidence clearly rules out structure (I) in which 3 different types of proton are present. Since the molecular weight of 168 as found from a mass spectrum is only consistent with a 2 : 4 ratio of diamine to formaldehyde, (II) is the only plausible alternative structure.

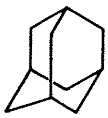
Construction of a model of (II) reveals several interesting structural features.† Firstly, the structure is clearly related to hexamethylenetetramine (III). Secondly, the sole symmetry element of the molecule is a fourfold alternating axis ($\bar{4}$ or S_4), which is comparatively rare. Thirdly, in order to account for the two singlets in the n.m.r. spectrum some rapid intramolecular process must time average the chemical shifts of each pair of geminal protons. Such a process is possible, and may be simulated in a Dreiding model by rotation about the carbon–carbon bonds in the ethylene bridges. The activation energy for this process must be low ($<$ 9 kcal mol^{-1}) as no kinetic broadening of the lines of the n.m.r. spectrum of a methylene chloride solution was observed at $-90°$.

The remote possibility that the molecule could exist with the methylene groups eclipsed in the ethylene bridges can be ruled out by the observation of triplets for the ^{13}C satellites of the high-field ethylene resonance with a splitting of 7·0 $\pm$ 0·2 Hz.


(I)


(II)


(III)


(IV)

To confirm our assignment of structure (II) to this compound we have performed a preliminary *X*-ray analysis. The cell dimensions and space group of the crystalline material have been determined. The space group is *I4mmm*, *I4mm*, *I*422, or *I*$\bar{4}$*m*2, and there are two molecules per unit cell. The first three can almost certainly be ruled out as the crystals show $\bar{4}2m$ symmetry. This requires the symmetry of the molecule in the crystal to be $\bar{4}2m$ (D_{2d} in Schoenflies symbols). There are three conceivable ways in which this may arise: (i) An arrangement with the methylene groups eclipsed in the ethylene bridges. This is very unlikely since one expects relatively small intermolecular forces in the solid which should not be sufficient to distort the arrangement already demonstrated in solution. (ii) A distribution in the crystal of molecules of $\bar{4}$ symmetry which gives rise to an overall symmetry of $\bar{4}2m$. (iii) An intermolecular inversion process occurring in the solid, similar to that occurring in solution.

---

† The reader is recommended to construct a Dreiding model of the molecule in order to follow the subsequent arguments.

Support for (iii) was obtained by differential scanning calorimetry on the crystalline material. This shows a relatively sharp first-order transition at −97°. This compares very closely with the similar compound adamantane (IV) which has a first-order transition at −65°.[6] This latter transition has been attributed to the onset of rotation of the approximately spherical molecules, suggesting that directional crystal packing forces are small in this type of molecule. The low energy barrier for inversion of (II) in solution is therefore likely to be little changed in the solid.

Since several molecules of structural type (I) have been reported we are re-examining their structures. A full three-dimensional crystal structure of (II) is also in progress.

(*Received, July 6th*, 1970; *Com.* 1077.)

---

[1] C. A. Bischoff, *Ber.*, 1898, **31**, 3248.

[2] C. A. Bischoff and F. Reinfeld, *Ber.*, 1903, **36**, 35.

[3] R. J. J. Simkins and G. F. Wright, *J. Amer. Chem. Soc.*, 1955, **77**, 3157.

[4] H. Krassig, *Makromol. Chem.*, 1956, **17**, 77.

[5] "Heterocyclic Systems with Bridgehead Nitrogen," Part 2, ed. W. L. Mosby, Interscience, New York, 1961, p. 1313.

[6] E. F. Westrum, *J. Phys. and Chem. Solids*, 1961, **18**, 83.