Structure of the Tetra-azacyclotetradecadiene formed from Benzylideneacetone and Ethylenediamine; X-Ray Crystal Structure Analysis of its Reduction Product

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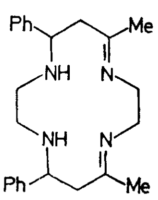
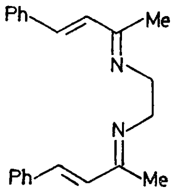
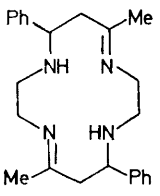
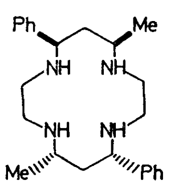
Summary An *X*-ray crystallographic examination of the sodium borohydride reduction product of the tetra-azacyclotetradecadiene obtained from benzylideneacetone and ethylenediamine shows that it has a *transoid* (5,12-dimethyl-7,14-diphenyl) structure.

When benzylideneacetone is heated with ethylenediamine in cyclohexane–ether in the presence of potassium carbonate a tetra-azacyclotetradecadiene is formed, which on mechanistic grounds was assigned a *cisoid* structure (I).[1] Support for this formulation was later obtained by showing that when this compound was heated in chloroform the bisenimine (II) was formed, and that this bisenimine reacted with ethylenediamine at room temperature to reform (I).[2]


(I)


(II)


(III)


(IV)

However, consideration of the stereochemistry of metal complexes of this macrocycle led other workers to suggest that, at least in the complexes, the ring might have an alternative *transoid* structure (III).[3] Confirmation of this suggestion came from an *X*-ray crystallographic examination of a copper(II) complex of the completely saturated reduction product of [(I) or (III)].[4]

Thus either the macrocycle had a *cisoid* structure (I) and underwent a reorganisation to a *transoid* form on metal complex formation, or it had the *transoid* structure (III) and on gentle thermolysis formation of (II) involved not only loss of ethylenediamine but also a reorganisation of the carbon skeleton, which was reversed when (II) recombined with ethylenediamine.

We now present evidence in support of the latter explanation and of the *transoid* structure (III) for the molecule.

The diene is readily reduced by sodium borohydride[1] to give a tetra-azacyclotetradecane which forms crystals which have been examined by *X*-ray crystallography and unequivocally have the *transoid* structure (IV). It seems unlikely that this gentle reduction should bring about a *cisoid–transoid* rearrangement so that the original diene must have a *transoid* structure also. Crystals of (IV) are monoclinic, space group $P2_1/c$ with four molecules of $C_{24}H_{36}N_4$ in a unit cell of dimensions $a = 7{\cdot}790(3)$, $b = 17{\cdot}991(7)$, $c = 16{\cdot}566(8)$ Å, $\beta = 102{\cdot}66(4)^\circ$. Using Mo-$K_\alpha$ radiation, 2430 reflexions were measured with a Hilger and Watts Y-290 four-circle diffractometer and the θ–2θ scan method. The structure was solved by direct methods and

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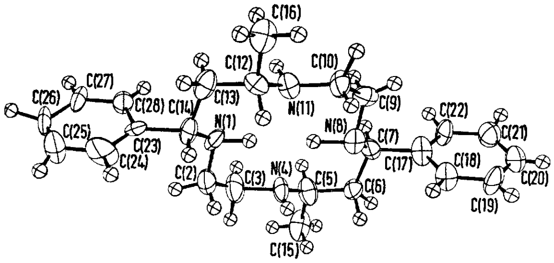
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

refined by full-matrix least-squares calculations. The conventional R-factor is 0·081 for 1011 'observed' reflexions.



FIGURE

A view of the molecule is shown in the Figure. Within the precision of this experiment, the centrosymmetric structure implied by (IV) is upheld in the crystal structure although the molecule does not occupy any of the available crystallographic centres of symmetry. All hydrogen atoms were located including those bonded to nitrogen. Two of these [those on N(1) and N(8)] are directed towards the ring centre and the others [those on N(4) and N(11)] are (*trans*) axial.

The unexpected reorganisation of the carbon skeleton seems most likely to involve initial retro-Michael elimination followed by intramolecular displacement of ethylenediamine; different detailed pathways can be drawn. Some initial further experiments[5] concerning both the formation and cleavage of the macrocycle show that the equilibria involved in both processes are complex.

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[3] D. F. Cook, N. F. Curtis, and R. W. Hay, *J.C.S. Dalton*, 1973, 1160; N. F. Curtis, *ibid.*, p. 1212.
[4] D. F. Cook, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 103.
[5] O. H. Hankovsky, K. Hideg, D. Lloyd, and H. McNab, unpublished results.