Structure of the Tetra-azacyclotetradecadienes obtained from α,β-Enones and Ethylenediamine

By Olga H. Hankovszky and Kálmán Hideg
(*Central Laboratory, Chemistry, University of Pécs, Pécs, Hungary*)

and Douglas Lloyd and Hamish McNab
(*Department of Chemistry, Purdie Building, University of St. Andrews, St. Andrews, Fife*)

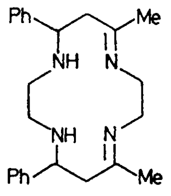
Summary The tetra-azacyclotetradecadiene obtained from ethylenediamine and benzylideneacetone has the *cisoid* structure (I) while that obtained from ethylenediamine monoperchlorate and mesityl oxide has the *transoid* structure (IV).

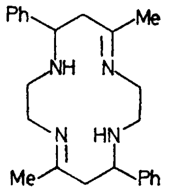
When ethylenediamine reacts with arylideneacetones a fourteen-membered ring compound, *e.g.* (I), is formed.[1] The *cisoid* structure (I) was preferred to the *transoid* structure (II) on mechanistic grounds; it was assumed that the diamine first added to two molecules of enone and the resultant diketone then cyclised by reaction with another molecule of diamine.

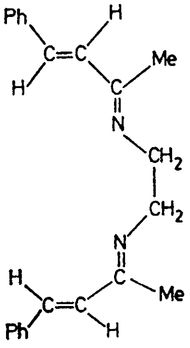
It has since been suggested,[2] from consideration of the stereochemistry of metal complexes which it forms, that this compound has structure (II) rather than (I). We now present evidence that the correct structure is indeed the *cisoid* form (I).

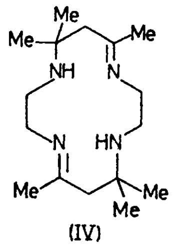
When (I) is heated in solvents such as chloroform or ethanol for 1—3 h it dissociates into ethylenediamine and a bisenimine, m.p. 112—113°, which from its mol. wt. (316), elemental analysis, and n.m.r. spectrum, τ ($CDCl_3$), 2·4—2·9 (m, 10H), 3·04 (AB, *J* 17 Hz, 4H), 6·18 (s, 4H), and 7·89 (s, 6H), must have structure (III). If this bisenimine is kept at room temperature with 1 equiv. of ethylenediamine it is reconverted into the cyclic compound (I). Formation of (III) and its reconversion into (I) is consistent only with structure (I) and not with the isomeric structure (II).

This thermal reverse Michael reaction is also evident in the mass spectrum of compound (I), wherein the base peak appears at *m/e* = 316 [≡(III)] which is also consistent with its formulation as (I).


(I)


(II)


(III)


(IV)

The diperchlorate of the analogous cyclic compound made by reaction of ethylenediamine monoperchlorate with mesityl oxide[3] has been assigned the *transoid* structure (IV) from its conversion into a metal complex of known structure.[3,4]

We have also evidence that this *transoid* structure is correct from the mass spectrum of the base derived from the diperchlorate on treatment with alkali. This gives the correct molecular ion peak ($M = 280$) but no breakdown fragment corresponding to loss of ethylenediamine, a reaction which would be expected had (IV) a *cisoid* structure analogous to (I). Rather, peaks due to the loss of Me_2CNH and $Me_2CNH{\cdot}(CH_2)_2{\cdot}NH$ fragments appear.

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