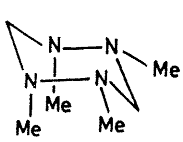
The Conformational Equilibrium of 1,2,4,5-Tetramethylhexahydro-1,2,4,5-tetrazine[1]

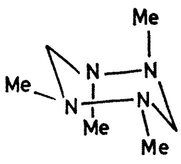
By RICHARD A. Y. JONES, A. R. KATRITZKY,* and A. C. RICHARDS
(*School of Chemical Sciences, University of East Anglia, Norwich,* NOR 88C)

Summary The title compound is predicted to exist predominantly in conformation (II), and this is confirmed by dipole moment measurements.

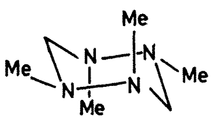
ANDERSON and ROBERTS[2] have recently studied the variable temperature n.m.r. of tetramethylhexahydrotetrazine. They show convincingly that this compound exists in a confirmation with two axial *N*-methyl and two equatorial *N*-methyl groups; of the three possibilities (I, II, III) they reasonably exclude (I) on steric grounds but they favour (III) over (II) for reasons which are not detailed in the preliminary communication. Following the work of Eliel,[3] we have suggested[4] that the free energy difference between conformers can be calculated by summing all of the interactions within each conformer, and comparing their sums: in the present instance such considerations clearly predict the predominance of (II) over (III): (a) Conformer (III) possesses two *gauche*-butane type interactions (H–C–N–N–C–H) between the two pairs of *N*-methyl groups, which is reduced to one in conformer (II). (b) Conformer (III) possesses two sets of *gauche* lone pairs on adjacent nitrogen atoms which will involve considerable dipole–dipole repulsion; conformer (II) has only one such interaction.† The effect of (a) is probably less than the 0·8 kcal. of the usual *gauche*-butane interaction because of easier angle



(I)



(II)



(III)

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† There is no entropy difference between conformers (II) and (III), since although (II) is a (±)-pair, it also has a symmetry number of 2.

deformation;[5] it is significant that the rotational barrier for 1,2-dimethylhydrazine[6] is only 3 kcal. compared to 6 kcal. for butane.[7] We estimate the effect of (b) as 0·9 kcal., using the equation derived by Lehn and Ourisson,[8] and assuming point dipoles of magnitude[5] 0·80 D located at the nitrogen atoms. The total effects of (a) and (b) are expected to favour conformer (II) by at least 1·2 kcal.; *i.e.* it should predominate to the extent of *ca* 90% in the equilibrium mixture.

The dipole moment of conformer (III) will be zero as it is centrosymmetric: we calculate the moments of conformers (I) and (II) as 2·47 and 1·31 D, respectively, on the following assumptions: (a) the individual dipoles contributed by the nitrogen atoms are 0·80 D as in 1-methylpiperidine;[5] (b) the tetrazine ring exists in the chair form; (c) the moment at each nitrogen atom is equally inclined to the *N*-methyl, the N–C, and the N–N bonds; (d) the angle between the lone pair axes on *vicinal* nitrogen atoms is 70 ± 5° (estimated from a model).

The observed dipole moment was 1·45 ± 0·01 D, measured in benzene at 25°, as previously described.[5] We conclude that tetramethylhexahydrotetrazine exists predominantly in conformation (II). The phenomenon of a methyl group preferring the axial position is by no means confined to this system.[9] In related work we have demonstrated that methyl groups frequently occupy axial positions in hexahydro-1,3,5-triazines[10] and sometimes in hexahydropyrimidines.[11]

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[1] For previous paper in this series, see R. W. Baldock and A. R. Katritzky, *J. Chem. Soc.* (*B*), 1968, **1470.**

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[3] *cf. e.g.*, E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, 1965, p. 446 ff.

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[6] J. G. Aston, G. J. Janz, and K. E. Russell, *J. Amer. Chem. Soc.*, 1951, **73**, 1943.

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[9] R. O. Hutchins, L. D. Kopp and E. L. Eliel, *J. Amer. Chem. Soc.*, 1968, **90**, 7174.

[10] R. A. Y. Jones, A. R. Katritzky, and M. Snarey, to be submitted to *J. Chem. Soc.* (*B*), (Hexahydropyrimidines).

[11] R. A. Y. Jones, A. R. Katritzky, and M. Snarey, to be submitted to *J. Chem. Soc.* (*B*), (Hexahydro-1,3,5-triazines).