

Conformational Interconversions in Acyclic and Cyclic Tetra-alkyl Hydrazines

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Summary The relationship between nitrogen inversion and rotation in acyclic and cyclic hydrazines is clarified and the temperature dependent n.m.r. spectrum of 1,2-dimethylhexahydropyridazine is reinterpreted.

THE n.m.r. spectrum of the tetramethyltetrahydropyridazine (**1**) shows three singlets at room temperature of area ratio 3:3:2 showing that ring and nitrogen inversions make the methylene and the *N*-methyl protons equivalent.¹ At -44° , the methylene protons become an AB quartet, a

process interpreted¹ as showing that (**1**) exists very largely in the two conformations (**2**) and (**3**) and involving the slowing down of nitrogen inversion (barrier $12.3 \text{ kcal mol}^{-1}$) but not of ring inversion. The temperature dependent changes of the n.m.r. spectrum of 1,2-dimethylhexahydropyridazine, involving a barrier of *ca.* 12 kcal mol^{-1} were interpreted¹ as demonstrating the existence of this compound very largely in conformations (**5**) and (**6**).

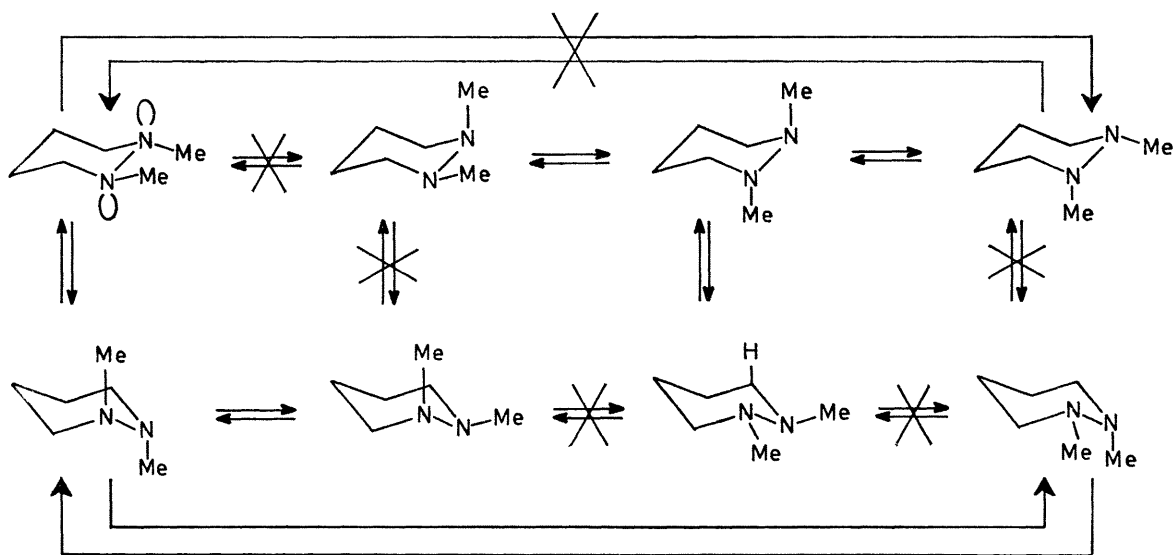
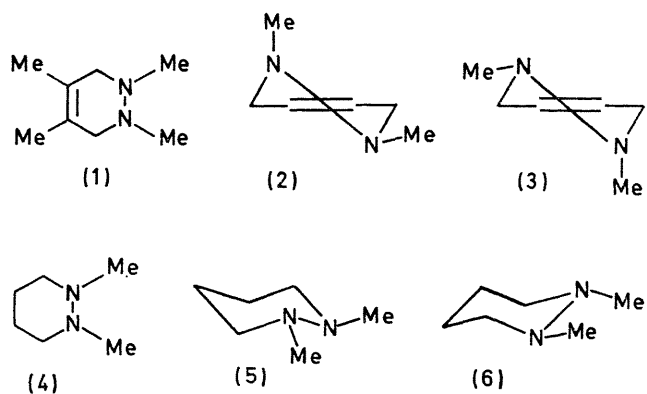
There are severe difficulties in these interpretations: it is unlikely that (**1**) or (**4**) exists very largely in any single

conformation, let alone that the preferred conformations should be of different types [*ae* for (1); *ee* for (4)]. In particular, we have shown² that for 1,2-dimethylhexahydropyridazine all the three types of *N*-methyl conformations (*aa*, *ee*, *ea*) are populated to a comparable extent. Finally, it is difficult to reconcile¹ the barrier postulated for *N*-inversion with those found for acyclic hydrazines³⁻⁶

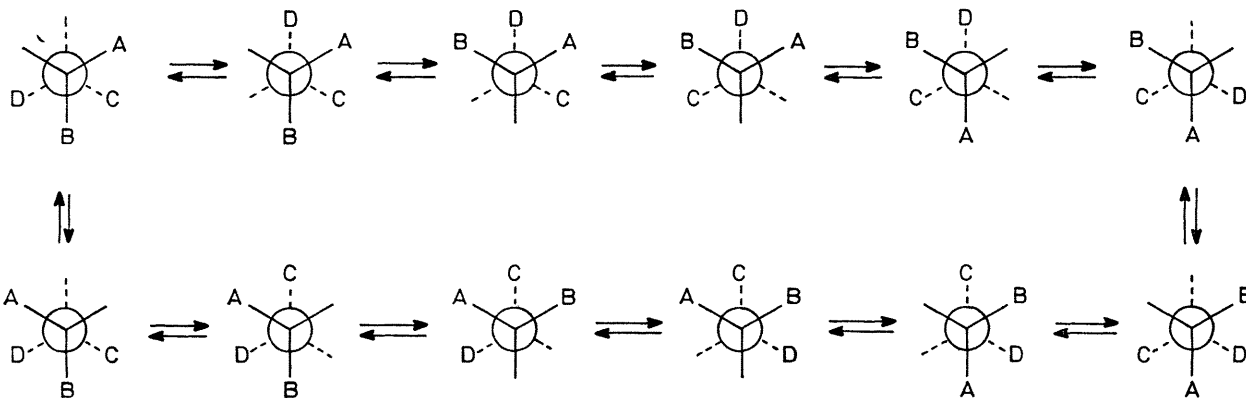
The possible conformations of 1,2-dimethylhexahydropyridazine are shown in Scheme 1: we believe that the barrier of *ca.* 12 kcal mol⁻¹ relates to the nitrogen inversions or ring inversions which involve a crossing of the two *N*-methyl groups. The eight conformations are divided by such processes into two equivalent sets of four; rapid equilibration within each set renders the *N*-methyl groups equivalent, but the hydrogens of the *N*-methylene groups are non-equivalent unless the two sets are undergoing rapid interconversion.

An acyclic hydrazine ABN·NCD can exist in 24 rotamers

Scheme 2. The rotamers within each set of 12 are interconvertible by successive nitrogen inversions which do *not*



SCHEME 1

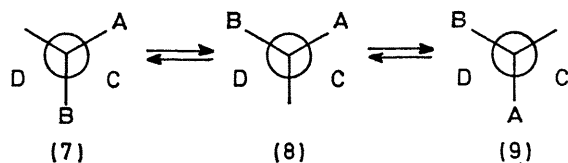


SCHEME 2

with gauche lone pairs: these fall into two sets of 12 in mirror image relationship, of which one set is shown in

involve two substituents passing each other. The barriers in tetrasubstituted hydrazines have previously^{3,5} been

interpreted as "inversion barriers" of *ca.* 8 kcal mol⁻¹ and "rotation barriers" of *ca.* 11 kcal mol⁻¹; inversion corresponds to processes of the type of Scheme 2, whereas rotation



is of type [(7) → (9)]. However, the process [(7) → (9)] can be considered as occurring by two inversions, each of which does involve substituents passing, *via* the intermediate (8). Thus the barrier for [(7) → (9)] should indeed be similar to the barrier found between the alternative sets in the cyclic compounds in Scheme 1.

Our work allows the reinterpretation of considerable further work concerning heterocyclic hydrazines (*e.g.* refs. 7, 1) as will be discussed in the full paper.

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¹ J. E. Anderson, *J. Amer. Chem. Soc.*, 1969, **91**, 6374.

² R. A. Y. Jones, A. R. Katritzky, D. L. Ostercamp, K. A. F. Record, and A. C. Richards, preceding communication.

³ J. R. Fletcher and I. O. Sutherland, *Chem. Comm.*, 1969, 706.

⁴ M. J. S. Dewar and B. Jennings, *J. Amer. Chem. Soc.*, 1969, **91**, 3655.

⁵ M. J. S. Dewar and W. B. Jennings, *Tetrahedron Letters*, 1970, 339.

⁶ J. E. Anderson, D. L. Griffith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 6371.

⁷ B. Junge and H. A. Staab, *Tetrahedron Letters*, 1967, 709.