

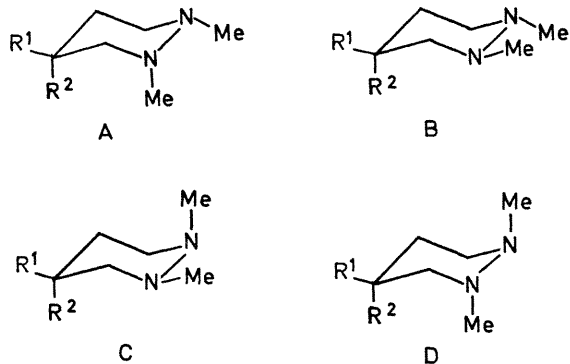
The Conformation of 1,2-Dimethylhexahydropyridazines

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Summary The three conformations of 1,2-dimethylhexahydropyridazine (methyl groups both axial, both equatorial, and one axial one equatorial) are approximately equally populated.

1,2-DIMETHYLHEXAHYDROPYRIDAZINE (1) exists in four conformations (A—D) of which two (A, C) are equivalent. In 1,2,4,4-tetramethylhexahydropyridazine (2), two conformations only (B, C) will be appreciably populated; in agreement, the 3,3,6,6-tetradeuterio-derivatives of (2) showed, at 183 K, two pairs of N—Me signals with areas in the ratio 2.7:1 indicating $\Delta G_{183}^0 = 0.361 \text{ kcal mol}^{-1}$ and, assuming that ΔH^0 is temperature independent and $\Delta S^0 = 0$, we deduce that $K_{298} = [2B]/[2C] = 1.8$. [Peak positions indicate that conformer (2B) is the more abundant]. The dipole moments of the di- and tetra-methyl compounds (1) and (2) are 1.49D and 1.06D, respectively. Assuming that the dipole moments of (1B) and (2B) are both zero, that



(1) $R^1 = R^2 = H$
 (2) $R^1 = R^2 = Me$

(3) $R^1 = Me; R^2 = p\text{-NO}_2\text{C}_6\text{H}_4$
 (4) $R^1 = p\text{-NO}_2\text{C}_6\text{H}_4; R^2 = Me$

those of all the other conformers [(1) and (2); A, C, and D] are equal to μ_g (all being dominated by the *gauche* lone-pairs), and that the ΔG^0 value between conformers (1B) and (1C) is the same as between (2B) and (2C), we calculate that the populations of conformers (1A), (1B), (1C), and (1D) are 17, 30, 17, and 36%, respectively.

To check this result, we studied the 4-methyl-4-*p*-nitrophenyl derivative [(3) \rightleftharpoons (4)]. We assume that the ΔG^0 difference between (3B) and (3C) is the same as that between (4B) and (4C). The equilibrium [(3) \rightleftharpoons (4)] was determined by low temperature n.m.r. which indicates $K_{298} = [4]/[3] = 0.76$. The dipole moment of [(3) \rightleftharpoons (4)], 4.66D, is considered to be derived from components arising from the aryl portion (equated to 4.69D, the measured moment of 1-methyl-1-*p*-nitrophenylcyclohexane) and the hydrazine portion (zero for conformers B and equated to μ_g for conformers C; conformers A and D are not significantly populated). Using standard bond lengths and angles we thus calculate resultant moments for each conformer, and hence derive $K_{298} = [3B]/[3C] = [4B]/[4C] = 1.8$. This value is identical to that derived for [2B]/[2C] from the low temperature n.m.r., which strongly supports the interpretations made.

The result is noteworthy for the large amount of the diaxial conformer (1D) that is disclosed; we believe that the energy of this conformer is lowered by distortion at the nitrogen atoms by bending the *N*-methyl groups away from the β -axial hydrogen atoms. Examination of models shows that such distortion moves the two *gauche* lone-pairs away from each other in (1D) but together in (1A) and (1C).

Our conclusions differ from those of Anderson,¹ who suggested from low temperature n.m.r. data that 1,2-dimethylhexahydropyridazine existed essentially completely as the diequatorial conformer (1B): his conclusion is not compatible with the appreciable dipole moment of this compound; however, reinterpretation² of the n.m.r. result is in good agreement with the present work.

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

² R. A. Y. Jones, A. R. Katritzky, and R. Scattergood, following communication.