HETEROCYCLES, Vol 21, No. 2, 1984

Barriers to Rotation and Inversion in meso-1,1'-Bi(2-methylpiperidine)s

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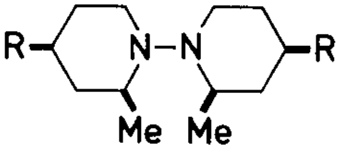
A ^{13}C DNMR study of meso-1,1'-bi(2-methylpiperidine) (1), meso-1,1'-bi(cis-2,4-dimethylpiperidine) (2), and meso-1,1'-bi(cis-4-tert-butyl-2-methylpiperidine) (3) with the aid of molecular mechanics calculation of the corresponding hydrocarbons 1,1'-bi(2-methylcyclohexane) (4), 1,1'-bi(cis-2,4-dimethylcyclohexane) (5), and 1,1'-bi(cis-4-tert-butyl-2-methylcyclohexane) (6) is reported. The most stable conformations of the bipiperidines are the enantiomeric conformations in which the lone pairs of the nitrogen atoms are approximately gauche to each other (G-SReeee and G+SReeee). In these conformations the N-N bond and all of the alkyl groups are equatorial to each of the chair form piperidine rings. The energy barriers ($\Delta G^{\ddagger}$) to the interconversion between these enantiomeric gauche conformations in 1, 2, and 3 are 12.5 (-25 °C), 17.7 (+72 °C), and 19.0 kcal mol^{-1} (+97 °C), respectively. While the barrier for 1 is assigned to the passing inversion of the nitrogen atoms, the barriers for 2 and 3 are assigned to the single-passing rotation about the N-N bond. In the case of 1, the next stable conformations, in which one of the methyl groups is axial, were observed at the lower temperatures. The free energy difference between the next stable and the most stable conformations is 0.55 kcal mol^{-1} at -117 °C and the energy barrier between these conformations is 9.2 kcal mol^{-1} at -82 °C, which is assigned to the ring inversion.



1 : R=H
2 : R=Me
3 : R=tert-Bu