Recognition of Paired Gauche^P–Gauche^M Sequences as the Source of the Rotational Barrier in 2,2'-Dimethyl-1,1'-bipiperidines†

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The reported rotational barriers about the N–N bond in *meso*-4,4'-dialkyl-2,2'-dimethyl-1,1'-bipiperidines (1) have been attributed through molecular mechanics calculations to a novel central-bond staggered conformation wherein two sets of a g^+g^- sequence are inescapably locked to generate a novel situation of unusually high energy.

The determination of rotational barriers about the N–N bond in alkylhydrazines has been hampered by concomitant inversion at the nitrogen atoms. Recently Ogawa et al.[1] devised an ingenious system in (1) capable of freezing out the inversion.

When R = H, the observed low energy process ($\Delta H^{\ddagger}$ 52 kJ mol^{-1} from dynamic n.m.r.) was attributed to a 'single passing inversion of the N atom' [equation (1), a–b, a'–b' = 2-Me-piperidyl ring] involving chair-to-chair inversion of one of the piperidine rings. When R = alkyl, the ring inversion that would have caused unfavourable 1,3-diaxial interaction between the 2-methyl and 4-alkyl groups could be suppressed and the observed higher energy process ($\Delta H^{\ddagger}$ 74—79 kJ mol^{-1}) was assigned to a 'single passing rotation' around the N–N bond [equation (2)]. Although this latter value may seem reasonable when compared with the known barrier of 43 kJ mol^{-1} for the single passing N–N bond rotation in the less crowded N,N'-dimethylhexahydropyridazine {(2), equation (2), a–b' = [CH$_2$]$_4$, a' = b = Me },[2] we report here the results of molecular mechanics calculations on systems modelling (1), which surprisingly revealed that the transition state for the rotation of the N–N bond in (1) is probably not eclipsed as shown in equation (2), but staggered.

The force field we used in this study (MM2)[3] has not been parameterized for the N–N function, but parameters for

(1) R = H, Me, Bu^t (2)

(3)

(1)
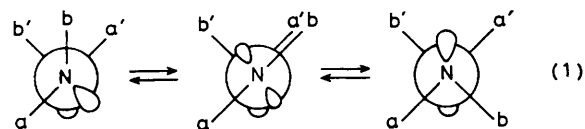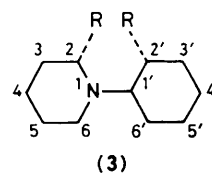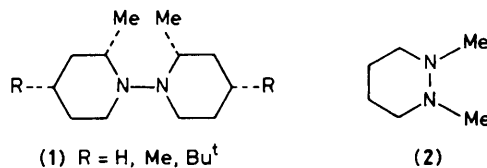
aliphatic amines have recently been implemented with the lone-pair as a quasi-atom.[4] Substituted N-cyclohexylpiperidines (3) may be considered as good models for (1) (C–N and N–N bonds have practically the same lengths of 1.44–1.46 Å).[5] 4- and 4'-substituents are not necessary because the nitrogen atom does not invert in molecular mechanics calculations.
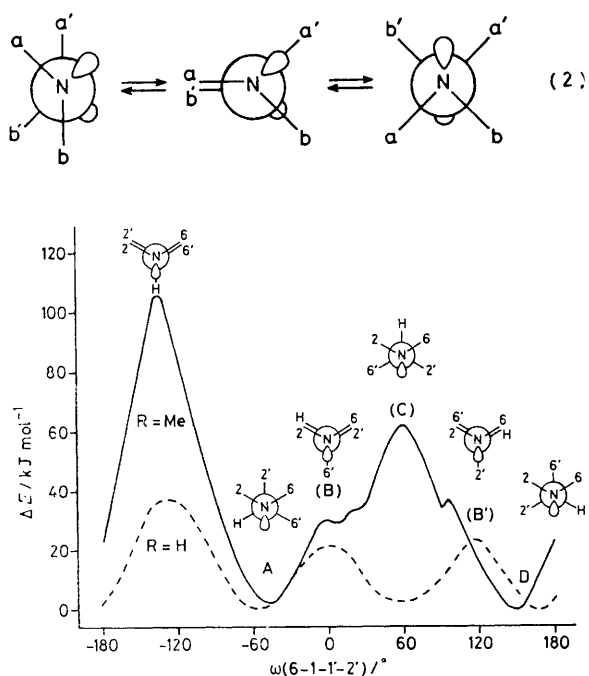
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(2)

Figure 1. Torsional energy curve obtained by driver calculations about the pivot bond of N-cyclohexylpiperidine [(3), R = H, dotted line] and the meso-2,2′-dimethyl derivative [(3), R = Me, solid line].

Figure 2. ORTEP drawing of the calculated transition state structure (C) of (3). Values on the structure are bonded and non-bonded distances in Å, and valence angles in degrees.

Driver calculations about the pivot bond of N-cyclohexyl-piperidine itself (3) (R = H) gave a torsion curve (Figure 1, dotted line) similar to that of 2,3-dimethylbutane.[6] The peaks at (B) and (B′)‡ correspond to the 'single passing barrier',[1] but they are very low. Introduction of branching at C(2) and C(2′) [(3), R = Me, Figure 1, solid line] leads to an increase of only 10 kJ mol⁻¹ at (B) and (B′), and brings the relative steric energies at these points to only 30 kJ mol⁻¹, which accounts for less than half of the observed barrier height for (1) (R = alkyl). A new and distinct barrier appeared at (C), where the C(6)–N(1)–C(1′)–C(2′) dihedral angle is 60°, and substituents around the pivot bond are all staggered. The height of the new barrier (C) is close to the experimental values for (1) (R = alkyl). The difference of ca. 15 kJ mol⁻¹ is probably due to the inadequacy of our model (3) (R = Me). In MM2, the C–C–C bending force constant is 40% smaller than the C–N–C bending constant,[3b,4c] and hence the C atom of (3) that replaced one of the N atoms in (1) must have absorbed strain more readily than that N atom.

Close inspection of the barrier (C) suggests a pair of g^+g^- arrangements involving Me–C(2)–N(1)–C(1′)–C(6′) and Me–C(2′)–C(1′)–N(1)–C(6), respectively, as the most important sources of strain. The double g^+g^- arrangements are locked into each other such that there is no way to avoid the strain. As a consequence, the nonbonded 1,7-H–H interaction between both ends of the g^+g^- unit is highly intensified as seen in the unusually short H–H distance, the decreased H–C_M–H angle, and the expanded valence angles around N, C(1′), C(2), and C(2′) (Figure 2). When only one g^+g^- sequence is present, as in A (Figure 1) or in monomethyl-(3) (R = H, Me), the molecule apparently is capable of dissipating the strain by suitable skeletal deformation.
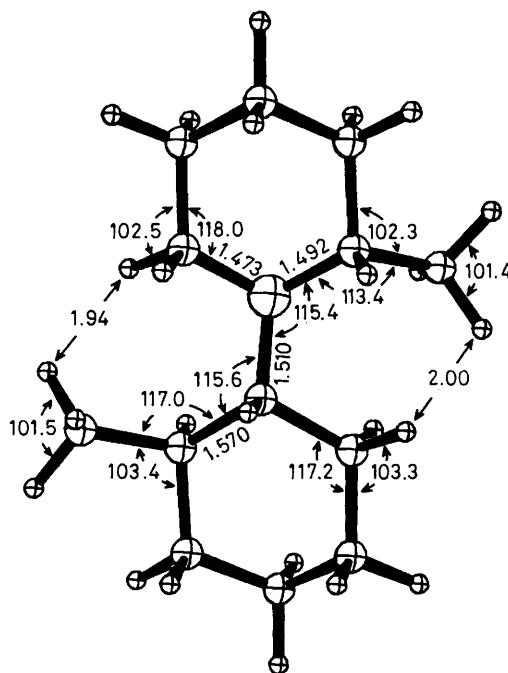
We confirm, then, the proposed single passing pathway of Ogawa et al. but with a rotational transition state shifted by 60° to (C) from the ones previously indicated at (B) or (B′).[1]

Previous interest in restricted rotation has concerned substituted ethanes where the highest barrier arises from eclipsing arrangements about the ethane bond.[7] To our knowledge, the reported activation process of (1) (R = alkyl) is the first example of such restricted rotation caused predominantly by long-range nonbonded interactions. For substituted bicyclo-hexyls and related molecules our work reveals further examples of an 'inescapably locked g^+g^- sequence'.

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‡ Letters in parentheses in Figure 1 denote saddle point conformations.