Barrier to Rotation about the N–N Bond in 1,1′-Bipiperidine

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Summary A ^{13}C dynamic n.m.r. study of *meso*-1,1′-bi(*cis*-4-t-butyl-2-methylpiperidine) revealed that the barrier to the single-passing rotation about the N–N bond was 79 kJ mol^{-1}.

THE energy barrier to rotation about the N–N bond in tetra-alkylhydrazines has never been unambiguously determined, because the conformational interconversion caused by rotation about the N–N bond can also be brought about by nitrogen inversions.[1] Our previous work has shown that introduction of *cis*-4- and -4-'methyl groups to *meso*-1,1'-bi(2-methylpiperidine) (**1**) selectively raises the barrier to the nitrogen inversion pathway without influencing the transition state of the rotation pathway and that the barrier to the single-passing rotation about the N–N bond (a rotation which involves eclipsing of only one pair of substituents in the transition state) was at least 74 kJ mol^{-1}, the barrier value ($\Delta G_c^{\ddagger}$) observed for *meso*-1,1'-bi(*cis*-2,4-dimethyl-piperidine) (**2**).[2]

To determine the barrier to the single-passing rotation about the N–N bond by dynamic n.m.r. spectroscopy, the selective perturbation must be such that the barrier to the nitrogen inversion pathway is higher than the barrier to the single-passing rotation pathway. One such perturbation is the introduction of 4-t-butyl groups instead of 4-methyl groups. Thus, in the present work we carried out a ^{13}C dynamic n.m.r. study of *meso*-1,1'-bi(*cis*-4-t-butyl-2-methyl-piperidine) (**3**),† which study provided the first definite value for the barrier to the single-passing rotation about the N–N bond in acyclic tetrasubstituted bipyramidal hydrazines.

In the noise-decoupled ^{13}C n.m.r. spectra (22·5 MHz, JEOL-FX-90Q spectrometer) of (**3**) in $[CD_3O(CD_2)_2]_2O$ all the peaks except those of the methyl carbons of the t-butyl groups split into two peaks of equal intensity as the temperature was lowered. The free energy of activation for the rate process was calculated from the exchange rates at the coalescence temperature (see the Table for results).

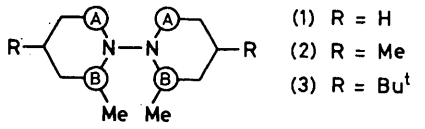
TABLE. Spectral data for (**3**) and free energy of activation ($\Delta G_c^{\ddagger}$) estimated at the coalescence temperature (T_c).

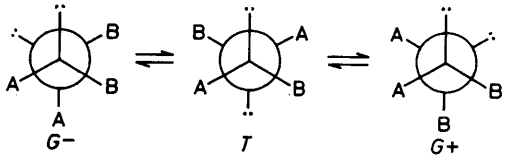
Position	$\Delta\nu$/Hz	T_c/°C	$\Delta G_c^{\ddagger}$/kJ mol^{-1}
2,2'	47·9	[a]	
6,6'	306·2	[a]	
3,3'	19·0	97	79·8
5,5'	7·3	80	78·8
$-C(CH_3)_3$	3·9	[a]	
4,4'	21·5	[a]	
$-C(CH_3)_3$	0·0		
2-Me, 2'-Me	41·0	105	79·1

[a] T_c was not determined.

† The synthesis of (**1**) will be reported in a full paper.

It is established that in the most stable conformation of 1,1'-bipiperidine the unshared electron pairs of the nitrogen atoms are *gauche* to each other with the N–N bond equatorial to both the piperidine rings.[3] Hence, the most stable conformations of (**3**) are certainly the enantiomeric *gauche* conformations *G*− and *G*+ shown in the Scheme.





SCHEME

The observed rate process corresponds to the interconversion of *G*− and *G*+.

The interconversion of *G*− and *G*+ is formally possible by various pathways. Among them the lowest barrier path should, according to the previous work,[2] involve the most stable of the *trans* conformations, *T*, in which the N–N bond is equatorial to both the piperidine rings with all the alkyl groups equatorial. The nitrogen inversion pathway, which must be accompanied by ring inversion, is unfavourable because ring inversion is severely inhibited by the 4-t-butyl groups. Hence, only one possible pathway which involves *T* is the single-passing rotation pathway.

Therefore, we conclude that the observed $\Delta G_c^{\ddagger}$ value of 79 kJ mol^{-1} for (**3**) is the barrier to the single-passing rotation about the N–N bond.

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