Conformational Changes in Heterocyclic Systems of the Bicyclo[4,4,0]decane and Bicyclo[3,3,0]octane Types*

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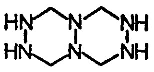
CONSECUTIVE inversion of the two nitrogen atoms in bicyclic hydrazine derivatives such as (I) has been studied recently by means of variable-temperature n.m.r. spectroscopy.[1] Conformational rate processes have also been found in other cyclic hyrdazine derivatives.[2,3]

We report here the observation of conformational changes involving nitrogen inversion, in compounds of the bicyclo[4,4,0]decane and of the bicyclo-[3,3,0]octane types: (II), (III), and (IV).

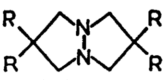
The n.m.r. spectrum (at 60 Mc./sec.) of the heterocycle (II)[4] in D_2O at 31° contains a single AB pattern centred at 3·6 p.p.m. (downfield from internal $Me_3Si\cdot[CH_2]_3\cdot SO_3Na$) for the ring CH_2 protons. A similar, somewhat sharper AB pattern is observed at $-6°$ with $\Delta\nu_{AB}$ 17·6 c./sec. and $J_{AB}=$ 11·9 c./sec. As the temperature is increased this pattern coalesces into a single line, the coalescence temperature being *ca.* 58 ± 2°. These changes are reversible when the temperature is lowered again.

The spectrum of compound (III)[5] is temperature-dependent and becomes much more complex at $-30°$ than it is at $+30°$. This result prompted us to study compound (IV) for which simpler spectral patterns are expected. The 60 Mc./sec. spectrum of (IV) at 31° in $CDCl_3$ solution shows two singlets at 1·20 and 2·77 p.p.m. (downfield from internal Me_4Si) with relative areas 2:3. As the temperature is decreased these signals broaden and at $-66°$ one observes an AB pattern centred at 2·85 p.p.m. ($\Delta\nu_{AB}$ 30·8 c./sec.; J_{AB} = 9·6 c./sec.) and a doublet at 1·23 p.p.m. (separation $\Delta\nu$ = 2·0 c./sec.). The low-field signals are attributed to the ring CH_2 protons and the high-field signals to the CH_3 protons. The coalescence temperatures (T_c) are $-29 \pm 2°$ and $-55 \pm 3°$ respectively for the low-field and the high-field signals.†

(I)



(II)



(III) R=H
(IV) R=Me

The temperature-dependent spectral changes observed for (II), (III), and (IV) point to the presence of a conformational rate process in these

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* Previous Paper in this series: P. Linscheid and J. M. Lehn, *Bull. Soc. chim. France*, in the press.

† The spectra show a marked solvent dependence. The splitting of the CH_3 doublet is a lower limit of $\Delta\nu$.

systems. From the values of $\Delta\nu$, J, and T_c the following free enthalpies of activation (ΔG^*_c) at T_c may be calculated, using Eyring's rate equation and a transmission coefficient of 1:

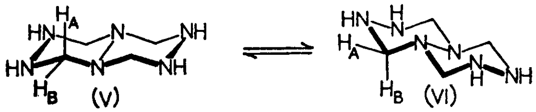
For compound (II) $\Delta G^*_{331} = 16{\cdot}6 \pm 0{\cdot}2$ kcal./mole

For compound (IV) $\Delta G^*_{244} = 12{\cdot}1 \pm 0{\cdot}2$ kcal./mole (from the CH_2 signals);

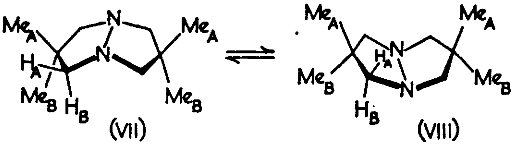
$\Delta G^*_{218} = 11{\cdot}95 \pm 0{\cdot}3$ kcal./mole (from the CH_3 signals).

If the conformation of (II) were of the *cis*-decalin chair–chair type, two AB patterns would be expected for the CH_2 protons; fast ring-inversion[6,7] (on the n.m.r. time scale) would lead to a single AB spectrum, and, if inversion of the ring junction also occurs, a single line is expected. A *trans*-decalin chair–chair form of (II) would give rise to a single AB pattern which, by fast inversion of the ring junction, would collapse into a single line. Furthermore, these *cis*- and *trans*-forms are interconvertible by inversion at the ring junction.

The observed coalescence of a single AB pattern into a single line implies that inversion of the nitrogen sites at the ring junction is occuring. The *cis*- and *trans*-decalin forms are then in equilibrium. However the *cis*-form is probably less stable than the *trans*-form[8] and should therefore be present in small amounts.‡ The *overall* conformational change giving rise to the spectral modifications observed for compound (II) may then be represented by a rate process of the type (V) ⇌ (VI) interconverting two conformations of the *trans*-decalin chair–chair type. Such a process involves inversion on the configuration at both nitrogen sites at the ring junction and ring inversion of the two chair forms.



Bicyclo[3,3,0]octane with a *trans*-ring junction is appreciably more strained than the *cis*-isomer.[8] Furthermore, in the *cis*-isomer of (IV) the conformation about the N–N bond is eclipsed, whereas the *trans*-N–N rotamer is present in the *trans*-isomer of (IV). According to the recent calculations on the barrier to internal rotation in hydrazine,[9] the eclipsed rotamer is expected to be substantially less stable than the *trans*-rotamer. It may be seen on molecular models that the conformation of (IV) with a *trans* ring junction has a twofold symmetry axis passing through the carbon atoms bearing the *gem*-dimethyl groups. One would therefore expect a singlet for the CH_3 protons at all temperatures, all four methyl groups being equivalent, and an AB pattern for the CH_2 protons. However in the *cis*-isomer of (IV) the two methyl groups on the same carbon atom are not equivalent and one expects a doublet for the CH_3 protons together with an AB pattern for the CH_2 protons. This is what is in fact observed in the spectrum of (IV) at −66°. The temperature-dependent spectral changes observed for (IV) [and for (III)] may then be attributed to the presence of a rate process of the type (VII) ⇌ (VIII) interconverting two forms with a *cis*-ring junction *via* inversion of both nitrogens at the ring junction.



The mechanism of these nitrogen inversion processes and the corresponding enthalpies and entropies of activation will be discussed in the final account of this work.

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‡ Torsional strain around the N–N bond should also be considered (see ref. 9) and may be somewhat smaller in the *cis*-form than in the *trans*-form. This point is being studied in the present systems as well as in systems of type (I) (ref. 1).

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[3] H. A. Staab, private communication.

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[9] A. Veillard, *Theor. Chim. Acta*, 1966, **5**, 413.