Double Inversion at Two Nitrogen Atoms in Bicyclic Hydrazines: A Carbon-13 Nuclear Magnetic Resonance Study

By Yujiro Nomura, Naruhito Masai, and Yoshito Takeuchi*

(*Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo, Japan*)

Summary Variable temperature ^{13}C n.m.r. spectra of bicyclic hydrazines reveal that the double inversion process at the nitrogen centres is *trans* ⇌ *trans* rather than *cis* ⇌ *cis*.

Double inversion at the two nitrogen atoms of cyclic and bicyclic hydrazines is of current interest.[1] *E.g.*, a variable temperature study of the ^{1}H n.m.r. spectra of compounds (**1**) and (**2**)[2,3] showed that the methyl or bridgehead proton signals, which are single peaks at room temperature, gradually broaden as the temperature decreases and finally split into two peaks. This might indicate that the double inversion (**3**) ⇌ (**4**) (*trans* ⇌ *trans*) which is fast at room temperature is frozen on the n.m.r. time scale. An alternative double inversion (**5**) ⇌ (**6**) (*cis* ⇌ *cis*) was excluded on the basis of the possible non-bonding interaction between the methyl groups or lone pairs on the two nitrogen atoms, and on the insensitivity of the chemical shifts of bridge methylene (H 7) protons to temperature variation.

Recently, the usefulness of ^{13}C n.m.r. spectroscopy in conformational analysis has been recognized.[4] Here we report a variable temperature ^{13}C n.m.r. study of compounds (**1**) and (**2**). The chemical shifts, δ (p.p.m. from Me_4Si), at 76 and −40 °C are summarised in the Table.† Assignments (76 °C) are based on the data for compounds (**7**) and (**8**),[5] which are also included in the Table. The effect of replacing a carbon atom in (**7**) or (**8**) with a nitrogen atom can be estimated by comparison of the δ values for

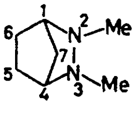
---

† Measured at 15 MHz with a JOEL 60-HL spectrometer for the neat liquid.

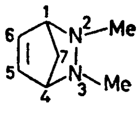
Table. Chemical shifts (δ) for compounds (**1**) and (**2**).[a]

Compound	Temp. (t/°C)	C-1 and -4[b] *endo*	*exo*	C-5 and -6[b] *endo*	*exo*	C-7	Methyl[b] *endo*	*exo*
(**1**)	76	65·1		26·6		34·8	43·0	
(**1**)	−40	63·1	64·6	21·0	30·2	33·9	39·3	45·2
(**2**)	76	69·2		135·4		44·3	43·8	
(**2**)	−40	67·8	68·6	133·4	137·6	43·4	41·5	44·8
(**7**)[5]	40	43·0	44·9	21·6	30·8	37·4	16·1	21·6
(**8**)[5]	40	48·9	49·8	133·2[c]	138·2[c]	47·0	18·6	20·4

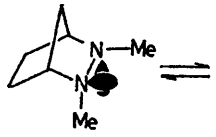
[a] Chemical shifts are based on external cyclohexane (76 °C) or n-pentane (−40 °C), and converted into δ values (p.p.m. from Me_4Si). [b] *endo* and *exo* indicate that the signal is due to the carbon on the same side as the *endo*- or *exo*-methyl group, respectively. [c] δ for C-2 and -3.



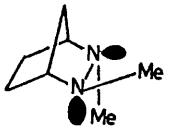
(1)



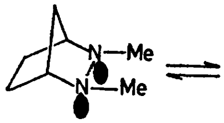
(2)



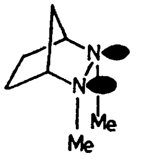
(3)



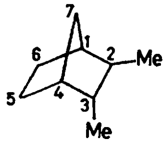
(4)



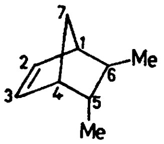
(5)



(6)



(7)



(8)

methylcyclohexane (**9**)[6] with those for N-methylpiperidine (**10**).[7] *E.g.*, the difference in chemical shift for C-2 between (**9**) and (**10**) is *ca.* 25 p.p.m.; hence the δ values for the N-methyl carbon atoms for (**1**) and (**2**) should be in the range 40—45 p.p.m., as observed.

As the temperature decreases, all the peaks for (**1**) and (**2**), except that for C-7, split into two peaks of equal intensity (Table). The δ values at 76 °C are the average of those for the two new peaks at −40 °C within experimental error.‡ Assignments for the new peaks were based on the steric compression effect proposed by Grant *et al.*,[6] *i.e.*, the chemical shifts for the carbon atoms on the same side as the *endo*-methyl group are assumed to be at higher field than the corresponding shifts of those on the same side as the *exo*-methyl group.

The C-7 peaks, however, remain as sharp singlets throughout the temperature range investigated (76 to −68 °C). Since freezing of the double inversion (**5**) $\rightleftharpoons$ (**6**) should give two peaks for C-7, and accidental degeneracy of the C-7 peaks for (**5**) and (**6**) is highly unlikely because the effect of the *endo*- and *exo*-methyl group on δ (C-7) in the norbornane system differs by *ca.* 5 p.p.m.,[5,8] our observation is unequivocal evidence that the process involved is (**3**) $\rightleftharpoons$ (**4**) rather than (**5**) $\rightleftharpoons$ (**6**).

(*Received*, 25*th January* 1974; *Com.* 098.)

---

‡ Probably because of different external standards (see Table) and because of possible temperature-shifts (of the sample and of the standard), δ(C-7) at 76 °C differs by *ca.* 1 p.p.m. from that at −40 °C for both (**1**) and (**2**). If such a correction is applied, the values at 76 °C for C-1 and C-4 are also an average of the two values at −40 °C.

[1] J. M. Lehn and J. Wagner, *Tetrahedron*, 1969, **25**, 677.
[2] J. E. Anderson and J. M. Lehn, *J. Amer. Chem. Soc.*, 1967, **89**, 81.
[3] E. L. Allred, C. L. Anderson, R. L. Miller, and A. L. Johnson, *Tetrahedron Letters*, 1967, 525.
[4] *E.g.*, A. J. Jones, E. L. Eliel, D. M. Grant, M. C. Knoeber, and W. F. Bailey, *J. Amer. Chem. Soc.*, 1971, **93**, 4772.
[5] E. Lippmaa, T. Pekh, J. Paasivirta, N. Belikova, and A. Platé, *Org. Magnetic Resonance*, 1970, **2**, 581.
[6] D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, 1967, **89**, 6612.
[7] G. Ellis and R. G. Jones, *J.C.S. Perkin II*, 1972, 437.
[8] J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7107.