

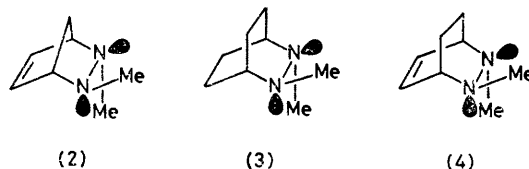
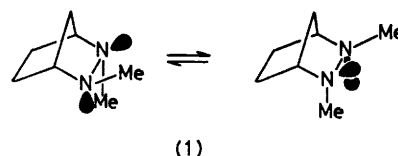
Double Inversion at Two Nitrogen Atoms in Bicyclic Hydrazines. A ^{15}N Nuclear Magnetic Resonance Study

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Summary Variable temperature ^{15}N n.m.r. spectra of bicyclic hydrazines are in accordance with *trans-trans* double inversion at the two nitrogen atoms and the estimated free energy of activation for inversion is in good agreement with the ^1H and ^{13}C n.m.r. results.

A NUMBER of ^{15}N chemical shifts of organic nitrogen compounds at the natural abundance level have recently been reported¹ and have been shown to be subject to structural influences which parallel, to a substantial degree, those which determine carbon chemical shifts.^{2,3} Previously *trans-trans* double inversion of the bicyclic hydrazine (1) and the related compounds (2)—(4) has been established by ^1H ⁴ and ^{13}C ^{5,6} n.m.r. (dynamic n.m.r.) spectroscopy. A ^{15}N dynamic n.m.r. study of these compounds would be of particular interest because of the scarcity of ^{15}N dynamic n.m.r. data, although the advantages of the method have been suggested.⁷ Thus, the natural abundance ^{15}N dynamic n.m.r. spectra of compounds (1)—(4) were determined.[†]



At 50 °C all the spectra exhibited a sharp, single peak while at -45 °C the peak split into two sharp peaks of equal intensity except for that of compound (3) where the two nitrogens remained equivalent even when the inversion

[†] ^{15}N Chemical shifts were measured with a JEOL FX-100 spectrometer operating at 10.09 MHz, for 1:1 (v/v) solutions in CDCl_3 . To obtain a signal-to-noise ratio of greater than 5:1, 400—3300 20° pulses were accumulated with a 2 s repetition rate.

TABLE. ^{15}N N.m.r. data for the bicyclic hydrazines (1)–(4)^a

Compound	$\delta/\text{p.p.m.}$ (at 50 °C)	Δ^b/Hz (at -45 °C)	T_c/K	$\Delta G^\ddagger/\text{kcal mol}^{-1}$		
				^{15}N n.m.r.	^1H n.m.r.	^{13}C n.m.r.
(1)	265.55	10.90	269+1	13.97 ^c	13.2 ^d	13.2 ^e
(2)	273.66	8.58	281+2	14.75 ^c	14.75 ^c	
(3)	281.64					
(4)	278.62	21.90	252+1	12.71 ^c	12.3 ^d	12.07 ^f

^a ^{15}N Chemical shifts in p.p.m. upfield from external $\text{NH}_4^{15}\text{NO}_3$ in D_2O . ^b Difference in the frequency of the two ^{15}N resonances. ^c This investigation. ^d Data taken from ref. 4. ^e Y. Nomura, N. Masai, and Y. Takeuchi, unpublished results. ^f Data taken from ref. 6.

was frozen out. This is in complete agreement with the ^1H and ^{13}C n.m.r. results. The chemical shifts and the differences in the chemical shifts for the two peaks are summarized in the Table. To the best of our knowledge this is the first direct observation of slow nitrogen inversion. The free energy of activation for inversion (ΔG^\ddagger) was estimated with the aid of the T_c (coalescence temperature) approximation.⁴ The T_c and ΔG^\ddagger values together with those determined by ^1H and ^{13}C dynamic n.m.r. spectroscopy are also included in the Table. The agreement among these values is within experimental error, establishing that ^{15}N dynamic n.m.r. spectroscopy is a potential means for the study of rate processes of nitrogen compounds.

Of the two peaks observed at low temperatures in the ^{15}N n.m.r. spectra of (1), (2), and (4), the higher field peak can tentatively be assigned to the nitrogen to which the methyl group which is *endo* with respect to the saturated [for (1)] or the unsaturated [for (2) and (4)] C–C unit is bonded if the correlation of carbon and nitrogen shifts is accepted.[‡] Because of the small chemical shift difference, however, the alternative assignment cannot be excluded.

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[‡] In the 'carbon' analogues of (1), (2), and (4) the *endo* methyl carbons always resonate at the higher field (see ref. 6 and E. Lippmaa, T. Pehk, J. Passivirta, N. Belikova, and A. Plate, *Org. Magnetic Resonance*, 1970, 2, 581.)

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