

SLOW NITROGEN INVERSION IN 7-AZABENZONORBORNADIENES

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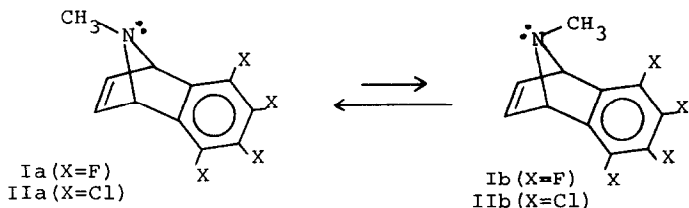
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We wish to disclose our preliminary studies concerning a new example of relatively slow nitrogen inversion.

At room temperature (22°) the 60 MHz nmr spectra of 7-methyl-7-azatetrafluorobenzonorbornadiene¹ (I) and 7-methyl-7-azatetrachlorobenzonorbornadiene² (II) show the expected proton absorptions: the sharp N-methyl singlet and the methine and vinyl multiplets. These parameters are summarized in Table I. As the temperature is lowered, the N-methyl, the methine, and the vinyl absorptions in I and II broaden and finally split each into two separate absorptions as shown in Figure I, for II. The original spectra are regenerated on warming to room temperature.

Due to the rigid nature of this ring system, the only rational explanation for these observations is the presence of slow nitrogen inversion on the nmr time-scale. Thus, in the temperature range of slow exchange on the nmr time-scale (ie., below the coalescence temperature, T_C) the two invertomers (eg., Ia and Ib) give rise to two distinct sets of chemical shifts for the three kinds of protons present. In the region of fast exchange (ie., above T_C)



the two invertomers give rise to a single set of time-averaged chemical shifts for the three different proton absorptions. The coalescence temperatures (T_C)

and chemical shift differences ($\Delta\nu$) are listed in Table I.

TABLE I. Spectral Parameters of I and II in DCCl_3 Solution at 60 MHz.^a

	<u>N-Me</u>	<u>Methine</u>	<u>Vinyl</u>
Chemical shift, 22°, I	2.18	4.88	6.98
Chemical shift, 22°, II	2.22	4.79	6.98
T_c , I	+1°	(-10°) ^b	(+2°) ^b
T_c , II	-2°	(-5°) ^b	(+2°) ^b
Chemical shift difference, ^c -40°, I	10.4	5.5	16.0
Chemical shift difference, ^c -50°, II	7.5	6.7	16.5
ΔF^\ddagger , kcal/mol, I	14		
ΔF^\ddagger , kcal/mol, II	14		

a. Chemical shifts are reported in ppm downfield from internal TMS and chemical shift differences are reported in hertz (Hz). Temperatures are in °C, are believed accurate to $\pm 2^\circ$, and were calibrated with a standard methanol sample prior to the measurement. b. These T_c 's were more difficult to assign and must be regarded as very tentative. c. Chemical shift difference between the centers of the multiplets of both invertomers.

Inspection of the spectra under conditions of slow exchange show that one invertomer is clearly favored over the second. Integration of the peaks (most accurately the vinyl proton absorptions at 100MHz) reveals an 83:17 invertomer ratio for I and a 75:25 ratio for II.

It is very tempting to suggest that the major conformation (invertomer) is the one having the lone pair on the same side as the electron-deficient benzene ring (ie., Ia and IIa) in an intramolecular charge-transfer interaction or π -complex.³ The observed trend is in accord with this electronegativity argument and not with a steric effect.⁴

Since the Gutowsky-Holm equation⁵ for calculating rate constants at T_c is only strictly applicable to conditions of equally populated sites, it cannot be applied with a high degree of confidence in the present case. However, it does permit a reasonable approximation and leads to a value of $\Delta F^\ddagger = 14$ kcal/mol for I and II at T_c using the N-methyl parameters (Table I) and the Eyring equation.

This activation free energy is lower than the N-alkyl,⁷ N-halo,⁸ and N-aminoaziridines⁹ but is comparable to or higher than known four-, five- and six-membered nitrogen heterocycles.^{8b,10}

The observed slow nitrogen inversion in I and II is not surprising since $sp^3 \rightarrow sp^2$ changes are known to be unfavorable at the 7-position in the norbornyl ring¹¹ and $sp^2 \rightarrow sp^3$ changes are known to be favorable.¹² Since nitrogen inversion involves an $sp^3 \rightarrow sp^2$ change the observed barrier is in accord with previous observations, and results from a strained sp^2 7-atom in the norbornyl ring (bond angle $\sim 96^\circ$) relative to the sp^3 7-atom.¹³

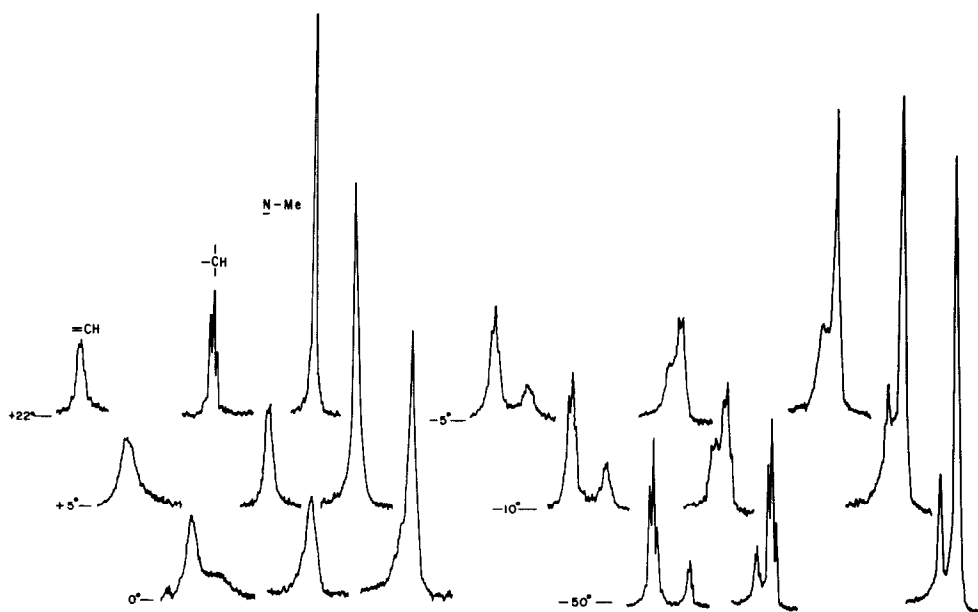


Figure I. The 60 MHz spectra of II at various temperatures in $DCCl_3$ solution. The three peaks are labeled as shown for the $+22^\circ$ spectrum. Spectra are offset to conserve space. Consult Table I for the chemical shifts.

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