

BARRIERS TO ROTATION AND NITROGEN INVERSION IN HYDRAZINES

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The barriers to rotation, and to inversion of nitrogen, in derivatives of hydrazine are of current interest¹. In a recent communication² we showed that the barriers to rotation about the NN bond in such compounds can be significant, and also that significant barriers exist to inversion of nitrogen, contradicting conclusions reached from a study of the microwave spectrum of hydrazine but in agreement with recent MO calculations³. Recently Fletcher and Sutherland⁴ have reported studies of the NMR spectra of various tetra-alkylhydrazines, which they took as evidence that the barriers to rotation are greater than those to inversion; these arguments, though strong, were not conclusive.

This ambiguity can be resolved by examining the methylene proton signals in the NMR spectra of compounds of the type $(\text{PhCH}_2)_2\text{NNR}_2$. With the accepted⁵ gauche conformation of the amino groups, the two benzyl groups can be non-equivalent if, and only if, both rotation about the NN bond, and inversion of NR_2 are slow on the NMR time-scale. On the other hand the protons of a given benzylic methylene can be non-equivalent if, and only if, inversion of the adjacent nitrogen atom is slow. Examination of the proton NMR spectra of such compounds therefore allows the relative rates of inversion and rotation to be compared.

The proton NMR spectrum* of tetrabenzylhydrazine (I) (Figure 1) exhibits a sharp singlet for the methylene protons at room temperature. As the temperature is lowered, the signal broadens, and below -100° it splits into two components with unequal intensities (ca 1:3). At -120° the signal at low field is

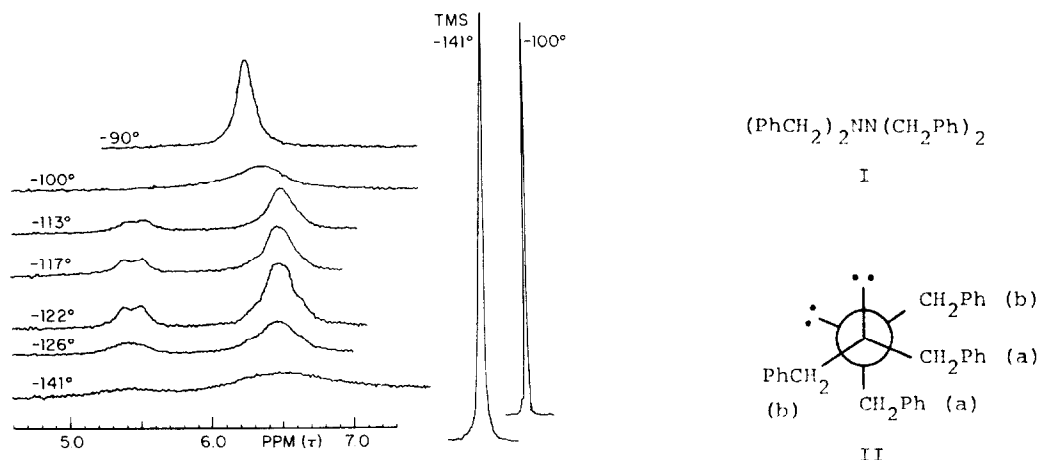


Figure 1. Proton NMR spectra of tetrabenzylhydrazine (I) in CH_2Cl_2 (5% w/v)

a broadened doublet, the ratio of this to the unresolved component at high field being 1:3. This suggests very strongly that both rotation and inversion have become slow on the NMR time scale, the molecule being frozen in the gauche conformation (II). In II there are two pairs of non-equivalent benzyl groups, i.e. "inner" (a) and "outer" (b); if nitrogen inversion is slow, the geminal protons of each methylene are also diastereotopic. The spectrum should then consist of two separate AB quartets, one for each type of benzyl group; the observed spectrum (Figure 1) is consistent with this prediction if one AB quartet is widely spaced (ca 1 ppm), the other closely, the unresolved high field signal corresponding to a superposition of the close AB quartet and one pair of lines from the widely spaced one.

If so, the fact that the signal broadens asymmetrically indicates that rotation is slower than inversion; for the benzyl groups can become nonequivalent only if both inversion and rotation are slow. If inversion were slower than rotation, the benzyl groups would remain equivalent in a temperature range where the protons of each methylene become non-equivalent; the proton signals

* All spectra were determined at 100 MHz on a Varian HA-100 spectrometer. Temperatures were measured using a calibrated copper-constantan thermocouple.

would then first split into a single symmetrical AB quartet. This behaviour was indeed observed** in the case of 1,1-dibenzylhydrazine² where inversion of the NH₂ group is likely to be rapid through proton tunnelling. Slow rotation alone cannot make the benzyl groups of I non-equivalent; if therefore rotation is slower than inversion, lowering the temperature will simultaneously both make the benzyl groups non-equivalent, and also make the methylene protons nonequivalent. Owing to the complexity of the spectrum and the broadness of the lines (see below), the barrier could not be measured accurately; however an estimate at the coalescence temperature (-105°C) is $\Delta G^\ddagger = 8$ kcal/mole, i.e. similar to that in III**. This suggests that the higher barriers observed by Fletcher and Sutherland⁴ (ca 11 kcal/mole) were indeed rotation and not inversion. We also studied the NMR spectrum of tetramethylhydrazine at low temperatures expecting the methyl groups to become non-equivalent; this, however, was not the case, no splitting being observed even at -150°C. The rotational barrier in II could well be due largely to steric effects.

The tertiary amine, dibenzylmethylamine (III) also exhibits slow nitrogen inversion at low temperature. The methylene protons occur as a broadened AB quartet at -150°C in vinyl chloride solution; $\Delta\nu_{AB} = 29$ Hz, $J_{AB} = 11$ Hz. At the coalescence temperature (-137°C), $\Delta G^\ddagger = 6.5$ kcal/mole. This is in good agreement with the barriers to inversion estimated for other tertiary amines in the gas phase⁶ and with the values calculated³ by the MINDO method, but it is significantly less than that ($E_A = 10.3$ kcal/mole) estimated by Saunders and Yamada⁷ for III in aqueous solution. The difference is probably due to the effects of hydrogen bonding.⁸

An unexpected observation, common to all the hydrazines we have studied, is the marked broadening undergone at low temperatures by the signals for hydrogen atoms α to nitrogen, or attached to nitrogen. This novel effect is due

** The spectrum of 1,1-dibenzylhydrazine in CHFCl₂-CF₂Cl₂ at -120° shows the methylene protons as a broadened AB quartet; $\Delta\nu_{AB} = 257$ Hz; $J_{AB} = 12$ Hz. Comparison of observed and calculated line shapes at the coalescence temperature (-106°C) gave $\Delta G^\ddagger = 8.0$ kcal/mole.

neither to instrumental defects nor to viscosity of the solvent; for the TMS and other reference signals remained sharp. Nor can it be due to N^{14} quadrupole relaxation because this should become faster⁹ at low temperature with a consequent narrowing of the proton signals. A similar broadening of the methyl signals was observed previously¹⁰ in the NMR spectra of certain dimethylamino-boranes at low temperatures; it was suggested that this might be due to slow rotation about CN bonds. It is therefore clear that broadening of NCH_2 signals at low temperature, without observing signal splitting, cannot be taken as strong evidence that nitrogen inversion is becoming slow on the NMR time-scale.

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