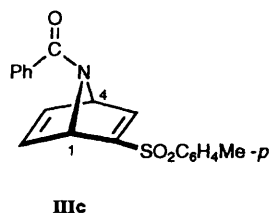


Hindered rotation about carbon–nitrogen bonds in 7-azanorbornadienes and their carbonyliron complexes*

A recent paper by Chow *et al.*¹ dealing with hindered rotation of carbon–nitrogen bonds presents variable-temperature NMR spectra which show the changes to the signals of the bridgehead hydrogens of the 2-tosyl-7-benzoyl amide **IIIc**. As the authors



point out in presenting their Fig. 1 (reproduced here), the larger pair of ¹H signals at δ 5.2 and 5.8 is derived from one conformer and the smaller pair from another. The spectra alter as the temperature rises and it is stated that 'the signals coalesce at 332 K.' (NB: the original caption says 523 K but this must be a mistake because the T_c is given as 50 °C in their Table 1). The signals which have been assumed to coalesce are those at δ 5.45 and 5.55 separated by 49 Hz in the spectrum measured at 500 MHz.

Examination of the spectra with a fresh eye reveals that the particular signals 1'' and 4'' merge, not with one another, but with the larger peaks 1' and 4' to produce the pair 1 and 4. The relative areas of signals 1' and 1'' (or 4' and 4'') indicate that the conformers exist in proportions of *ca.* 65:35 and the high-temperature signals occur at the positions of the weighted means of their constituents, δ 5.35 and 5.65, as anticipated. The assignment of the respective signals to the hydrogen atoms in positions 1 and 4 of structure **IIIc** was not explicit in the original paper but is justified by the observation that coupling to the non-equivalent hydrogens at positions 3 and 5 is responsible for the fine structure of peaks 4' and 4''. The existence of conformers in unequal proportions is to be expected in systems of this kind.²

In my experience it is difficult to judge the coalescence temperature when the merging signals are of unequal size,³ and careful inspection of the published series of spectra¹ favours the choice of 331 rather than 323 K. The separation of each small peak from its larger partner is 175 Hz, which yields $k_c = 390 \text{ s}^{-1}$ for the rate of exchange. These data lead to $\Delta G^\ddagger = 15.5 \text{ kcal mol}^{-1}$. This is a small but necessary amendment to the previously calculated energy of activation for **IIIc** of 16.0 kcal mol⁻¹. Results for some other 7-azanorbornadiene (7-azabicyclo[2.2.1]hepta-2,5-diene) derivatives¹ may also require correction but the necessary data are not available. A referee has pointed out that ideally the spectra should be re-run with temperature calibration and lineshape analysis so that the rotational barrier can be calculated more precisely.

In the paper under discussion some carbonyliron complexes are also examined by variable-temperature NMR spectroscopy. Only the bridgehead hydrogen resonances are followed to

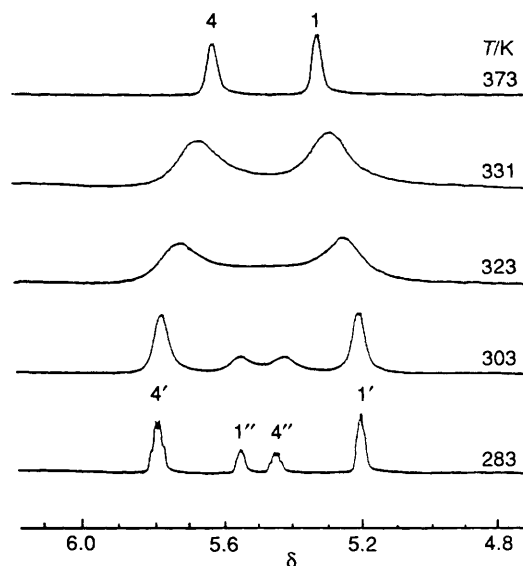
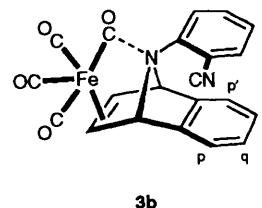


Fig. 1 Variable-temperature ¹H NMR spectra of the amide **IIIc**. Abridged from Chow *et al.*¹



derive the free energy of activation,¹ although the spectra of compound **3b** undergo marked changes in the aromatic region where two other pairs of signals (probably those of the hydrogens at positions p–p' and q–q') are seen to coalesce. Such evidence supports the assignment of the resonances to these particular hydrogen atoms. The additional coalescence data can be used to determine ΔG^\ddagger at two further temperatures and hence to estimate ΔH^\ddagger and ΔS^\ddagger for the process concerned, namely hindered rotation about the N–Ph bond of **3b**.

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* Non-SI unit employed: cal = 4.184 J.