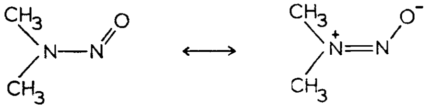
Vapour-phase Nuclear Magnetic Resonance Studies of Hindered Internal Rotation: Dimethylnitrosamine

By R. K. HARRIS and R. A. SPRAGG
(*School of Chemical Sciences, University of East Anglia, Norwich*)

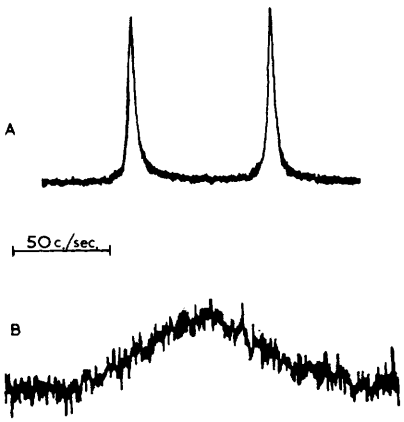
WE report the first n.m.r. measurement of a barrier to internal rotation in the vapour phase, thus allowing estimation of intra- and inter-molecular contributions to the barrier independently.

The compound concerned is dimethylnitrosamine; the barrier in the liquid phase has been studied by both steady state[1,2] and spin-echo[3] n.m.r. methods. This barrier (to rotation about the N–N bond) has been attributed to partial double-bond character produced by overlap between *p*-orbitals on the two nitrogen atoms.



We have measured the 100 Mc./sec. proton resonance spectrum of gaseous dimethylnitrosamine between 80 and 180°, in order to estimate the contribution of intra- and inter-molecular forces to the barrier to internal rotation. The sample was sealed in a 5 mm. (outside diameter) tube with tetramethylsilane (TMS) as an internal reference. In the temperature range studied there was a small excess of liquid dimethylnitrosamine in the sample, the partial presssure in the vapour being approximately the vapour pressure of the pure liquid, 1 atmosphere at 153°. The quantity of TMS was calculated to give a partial pressure of 10 atmospheres at 100° and 16 atmospheres at 180°. The high pressure of TMS was used in order to obtain narrow resonance lines,[4] and to provide a sufficiently intense signal to allow use of the field frequency locking system of the spectrometer, a Varian HA-100.

At 105° the spectrum consists of two peaks of equal intensity at τ 6·38 and 7·17, the line-widths being 4·5 c./sec. (compared with 1·9 c./sec. for the TMS peak). The peaks broaden as the temperature is raised, and coalescence occurs at 158°, the line-width of the TMS peak being 1·8 c./sec. at this temperature. At higher temperatures the spectrum consists of a single peak at $\tau = 6{\cdot}73$ (Figure). The free energy of activation, ΔG^*, for internal rotation is obtained from the coalescence temperature as 21·1 kcal. mole^{-1}. Inclusion of the effect of finite line-width,[5] *ca.* 5 c./sec., changes the value of ΔG^* by less than 0·1 kcal. mole^{-1}. The 100 Mc./sec. spectrum of the liquid at 160° is a



The 100 *Mc./sec. spectrum of dimethylnitrosamine at* 161°; (A) *in the liquid* (B) *in the vapour phase.*

well-resolved doublet with peaks at τ 6·28 and 7·02 (Figure), and the coalescence temperature is above 195°, the highest temperature at present obtainable with our spectrometer. From the reported coalescence temperature for the liquid at 40 Mc./sec., 183°,[1] the value of ΔG^* for the liquid is obtained as 23·3 kcal. mole^{-1}. (The reported coalescence temperature at 215° at 30 Mc./sec.[6] is incompatible with the published 40 Mc./sec. spectra,[1] and is presumably incorrect.) The intermolecular contribution to the barrier to internal rotation is therefore about 2 kcal./mole (only *ca.* 10% of the total), the barrier being higher in the liquid than in the vapour phase. There is little reported work on the measurement of barriers in liquid and vapour phases by the same technique; one example is benzaldehyde, far-infrared measurements for which indicate that the barrier to internal rotation is about 2 kcal. mole^{-1} greater in the liquid than in the vapour phase.[7] The observation that far-infrared frequencies are usually lower in the vapour phase than in liquids[8] is in agreement with the idea that torsional barriers are generally lower in gases than in liquids.

A further area in which vapour-phase n.m.r. measurements are of great interest is that of chemical-shift measurements. Here again intermolecular effects make it difficult to investigate intramolecular contributions by use of liquid-phase data. Estimations of the anisotropy of bond diamagnetic susceptibilities, for instance, are subject to considerable uncertainty when vapour-phase data are unobtainable (the utility of "inert" solvents can only properly be justified by comparison of vapour-phase and solution data). It is therefore interesting and (heartening) to note that the chemical-shift difference between the methyl groups *cis* and *trans* to the nitroso-group in dimethylnitrosamine is 0·79 p.p.m. in the vapour phase at 105°. This value is very close to that for a dilute solution in CCl_4 (0·794 p.p.m.) at room temperature, but significantly different from that for liquid dimethylnitrosamine (0·744 p.p.m., temperature independent between 30 and 160°). In this case, at any rate, use of data from CCl_4 solutions for deriving intramolecular parameters[9] is justified.

(*Received, February* 6*th*, 1967; *Com.* 112.)

[1] C. E. Looney, W. D. Phillips, and E. L. Reilly, *J. Amer. Chem. Soc.*, 1957, **79**, 6136.
[2] D. J. Blears, *J. Chem. Soc.*, 1964, 6256.
[3] K. H. Abrahamson, P. T. Inglefield, E. Krakower, and L. W. Reeves, *Canad. J. Chem.*, 1966, **44**, 1685.
[4] L. G. Alexakos and C. D. Cornwell, *J. Chem. Phys.*, 1963, **39**, 1616.
[5] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.
[6] W. D. Phillips, C. E. Looney, and C. P. Spaeth, *J. Mol. Spectroscopy*, 1957, **1**, 35.
[7] W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, 1965, **21**, 231.
[8] W. G. Fateley, I. Matsubara, and R. E. Witkowski, *Spectrochim. Acta*, 1964, **20**, 1461.
[9] R. K. Harris and R. A. Spragg, *J. Mol. Spectroscopy*, to be published.