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A NUCLEAR MAGNETIC RESONANCE TOTAL LINE-SHAPE TREATMENT OF INTERNAL ROTATION IN DIMETHYLFORMAMIDE

Alexander Pines and Mordecai Rabinovitz
Department of Organic Chemistry,
The Hebrew University of Jerusalem, Jerusalem, Israel

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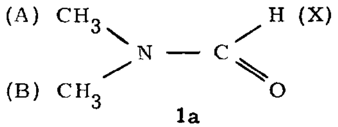
We have shown[1] that dimethylformamide (DMF) molecules exhibit strong polar interactions in solution. These interactions are of the order of 6 Kcal/mole and must have an appreciable influence on the process of internal rotation in these molecules. In order to discuss the nature and extent of any such perturbations, we clearly require an accurate method for examining the internal rotation in this system and determining the magnitude and reliability of the thermodynamic parameters associated with it[2].

Here, we describe preliminary results of a total nmr line-shape analysis of the hindered internal rotation in DMF; this method seems to be the only one meeting the above requirements. A computer was available and it was a simple matter to introduce the N-methyl-formyl proton coupling into the treatment, as well as the temperature dependence of the limiting N-methyl proton chemical shift[3]. However, the main advantage of this method is that it furnishes a direct check on the values of the parameters derived, by examination of the "closeness-of-fit" between the experimental and computer-generated theoretical nmr curves. Linearity of Arrhenius plots alone does not seem to be a sufficient criterion, as in many cases linear plots have been reported for the case of DMF, each leading to widely different values for the activation energy and frequency factor[4].



1a

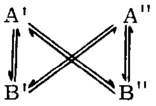
At room temperature, the N-methyl proton resonance spectrum of DMF consists of two closely spaced doublets A and B, due to coupling between the N-methyl and formyl protons, (**1a**); thus, A = (A', A"), B = (B', B").

$$\upsilon B - \upsilon A = \Delta\upsilon$$

$$\upsilon A'' - \upsilon A' = J_{AX}$$

$$\upsilon B'' - \upsilon B' = J_{BX}$$

1b



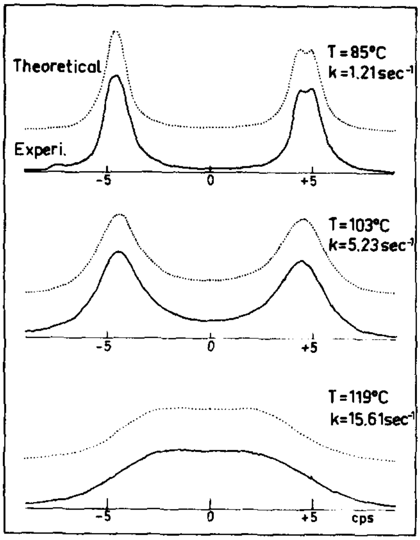
1c

We consider these resonances as due to four equally populated sites, and using the notation in **1b** regard the internal rotation as a combination of the exchange processes **1c**[5], with all transition probabilities equal to k/2 (where k is the rotation rate constant). An IBM 7040 digital computer was programmed with the Bloch equations[6] for an equally populated four-site system modified by the method of McConnell[7] to include the above exchange. The input to the program consists of T_2^{*-1} (half the natural line width), J_{AX}, J_{BX}, guessed initial values of the variable parameters $\Delta\upsilon$ and k, and a set of values for the absorption intensity at about 50 frequency points. Values of $\Delta\upsilon$ and k are then computed leading to a best-fit[8] between observed and predicted normalized intensities. Suitable values of T_2^{*-1}, J_{AX} and J_{BX} were calculated by preliminary analyses at low temperatures and taken as constants throughout the temperature range[9].

Using T_2^{*-1} = 0.3 cps, J_{AX} = 0.5 cps, and J_{BX} = 0.75 cps[10], the fits obtained in this manner were excellent, with less than 0.5 percent of the variation usually unexplained[8].

FIGURE 1.

Experimental (———) and computer-generated theoretical (. . .) nmr spectra for the N-methyl protons of DMF at three temperatures.
k is the rate constant of internal rotation.



For illustration, Figure 1 shows the experimental and computer-generated spectra at three temperatures, together with the corresponding values of the rate constant. The activation energy for hindered internal rotation derived from the least-squares Arrhenius plot is 20.5 ± 0.2 Kcal/mole and the frequency factor $(5 \pm 3) \times 10^{12}$ sec^{-1}. The error ranges are those of 90% confidence for these parameters[8]. The activation energy is similar to that encountered in other amides[3, 4(b)] and the "normal" frequency factor eliminates the necessity of postulating unusually high positive or negative entropies of activation for this particular compound[4(a), (b)].

Thus, this method yields accurate and seemingly reliable results, as expected (ref. 3), and seems to warrant its further application to study the general behavior of DMF in solution.

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10) These J values are identical with one set reported previously: G. Fraenkel and C. Franconi, J. Am. Chem. Soc., **82**, 4478 (1960).