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T. T. Bopp [a] & N. S. Balakrishnan [a]
[a] Department of Chemistry, University of Hawaii, Honolulu, Hawaii, 96822

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THE PROTON MAGNETIC RESONANCE SPECTRUM OF N,N-DIMETHYLFORMAMIDE IN A NEMATIC SOLVENT

T. T. BOPP AND N. S. BALAKRISHNAN
Department of Chemistry, University of Hawaii,
Honolulu, Hawaii 96822

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The proton magnetic resonance spectrum of N,N-dimethylformamide (DMF) oriented in a nematic solvent is analyzed. From the derived dipolar coupling constants and using the best available structure of DMF it is shown that the NMR results are consistent only with rapidly inverting nonplanar conformers.

INTRODUCTION

It is now well established that nematic phases provide a suitable anisotropic environment for dissolved molecules permitting high resolution nuclear magnetic resonance spectroscopy of solute molecules.[1] Although such studies in the past have been largely confined to solute molecules with considerable symmetry, in recent years the application of this technique has been extended to molecules with low symmetry and/or with groups executing large internal motions. However, a limitation of the method is that for the determination of geometrical information from the NMR spectra of oriented systems, the number of dipolar coupling constants (D_{ij}'s) obtainable from spectral analysis must be larger than the number of order parameters required for a definition of the solute orientation and the number of coordinates required for a specification of the relative positions of the interacting magnetic nuclei in the molecule.[2]

The conformations of peptides and proteins have attracted the attention of various workers. Although some

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theoretical calculations of peptides have been based on a planar model, this assumption of the coplanarity of the three bonds meeting at the nitrogen atom in a peptide unit is questionable and attention has been called to a need for considering nonplanar distortions.[3] The technique of anisotropic NMR spectroscopy in liquid crystal solvents can be used to probe the planarity-nonplanarity problem[4] and recently Khetrapal and coworkers have focused attention on some simple monosubstituted amides.[5,6] In this communication, we report the analysis of the PMR spectrum of N,N-dimethylformamide (DMF), the simplest disubstituted amide and provide an estimate of the nonplanar distortions around the nitrogen atom.

EXPERIMENTAL

Figure 1A shows the 100 MHz PMR spectrum of ∿ 20 mole % DMF in an eutectic mixture of butyl p-(p-ethoxyphenoxycarbonyl) phenyl carbonate (∿ 60 mole %) and p-(p-ethoxyphenylazo) phenyl valerate (∿ 20 mole %). The spectrum was recorded on a Varian XL-100 spectrometer, operating in the Fourier transform mode. The sample was monitored until a constant spectral width was obtained to ensure adequate thermal equilibrium.

SPECTRAL ANALYSIS

The spectrum was analyzed according to standard procedures[7] using a version of the LAOCOON 2 program modified to include dipolar couplings. During the analysis, both the chemical shifts, $(\nu_i - \nu_j)$ and the dipolar coupling constants (D_{ij}'s) were simultaneously varied. The spin-spin coupling constants (J_{ij}'s) were taken from the isotropic results of DMF.[8,9] Line assignments were made by fitting 89 lines to 257 transitions with an rms error of 1.9 Hz. The spectral parameters are listed in Table 1. The "probable errors" in the chemical shifts and coupling constants were estimated as 0.2 Hz.

RESULTS AND DISCUSSION

The order matrix $\underset{\sim}{S}$ for a planar molecule is specified by three independent elements.[1] Since the PMR spectrum of DMF furnishes five independent dipolar couplings, a maximum of two pieces of structural information may be obtained. Thus some assumptions must be made about the structure and internal motions of the molecule.

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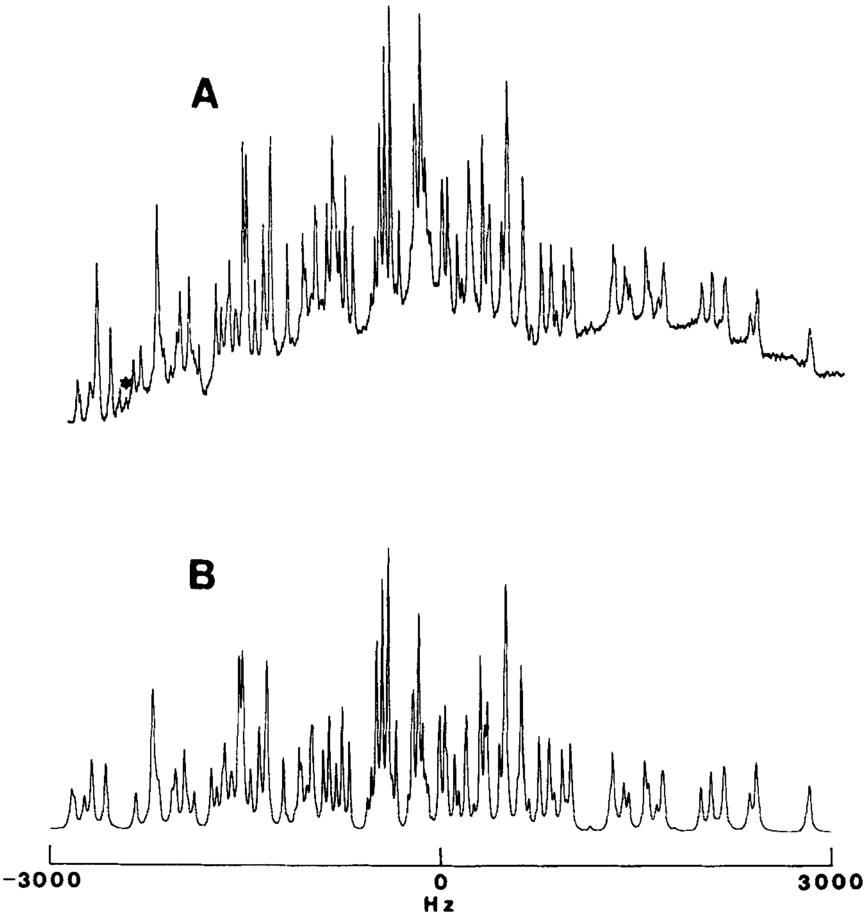

FIGURE 1

Observed (A) and calculated (B) 100 MHz N.M.R. spectra of partially oriented DMF. Concentration, 20 mole percent; temperature ∿ 35°C. The two peaks flanking the asterisk symbol in (A) are "fold-over" peaks, from some intense lines falling outside the spectral width. (B) is calculated with a varying linewidth: 15 Hz at the center, and increasing by 5 Hz for every 1000 Hz away from the center of the spectrum.

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TABLE 1

100 MHz NMR Spectral Parameters (in Hz) of Partially Oriented DMF

J_{47}	0.4	D_{12}	431.9
J_{17}	0.9	D_{45}	793.5
J_{14}	0.0	D_{47}	-373.7
$\nu_7-\nu_1$	-482.8	D_{17}	-71.2
$\nu_4-\nu_1$	+1.8	D_{14}	-168.0

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There are no structural data on DMF itself except for a 1962 electron diffraction study.[10] However, microwave data on formamide[11], x-ray[12], electron diffraction[13] results on N-methylacetamide and an x-ray structure determination of a 1:1 molecular complex formed between 1,7 diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and DMF[14] are available. Based on the structures of these model compounds, the molecular geometry was assumed to have the bond angles and bond distances indicated in Figure 2b. The $H\hat{C}H$ angle within the methyl groups was assumed to have the regular tetrahedral value of 109.5°. Furthermore, the N-C' and N-C" bond lengths were assumed to be equal. The angles varied in this study are the out-of-plane angles ε and ω which the N-C"H_3 and N-C'H_3 bonds make with the symmetry plane respectively (Figure 2a). That ε and ω might be unequal is suggested by the reported non-planar structure for formamide,[11] in which the corresponding angles have values of 12 and 7 degrees, respectively.

The dipolar couplings observed in NMR are averages over all rapid internal motions of the molecule. The inversion at the nitrogen atom is expected to be rapid.[15] Since two chemically shifted "fully equivalent"[16] methyl groups are observed, rotation about the C-N bond is slow while rotation of each methyl group (about the C'-N or C"-N bonds) is rapid.

The two out-of-plane angles ε and ω were found by direct search. Values for ε and ω, along with an assumed model for the methyl group rotation, were combined with the five experimental dipolar coupling constants to set up the least-square normal equations. These were solved for the "best-fit"

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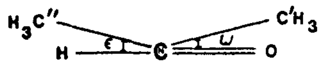

Figure 2(a)

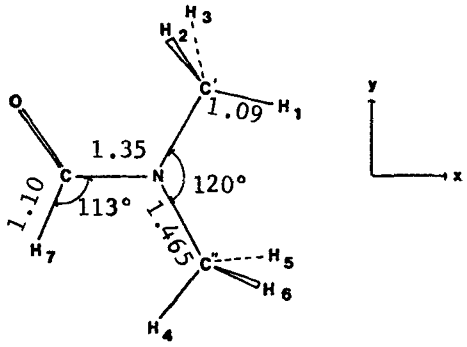

Figure 2(b)

FIGURE 2(a) One of the two equilibrium positions for the inversion of the methyl groups through the effective molecular plane. The angles ε and ω describe the nonplanar distortions about the nitrogen.

FIGURE 2(b) Coordinate system and assumed structure of DMF, using the geometrical data of model compounds.[10-14] Bond distances are in Å. Shown is the "staggered-eclipsed" rotomer.

values of S_{xx}, S_{yy}, and S_{xy}, and the rms deviation of the calculated, D_{ij}'s from the experimental D_{ij}'s was recorded. The angles ε and ω were then systematically varied until this rms error for the calculated set of dipolar couplings was minimized. No correction for molecular vibrations was made.

The resulting values for ε and ω depend on the model used to describe the methyl rotation. This is not surprising, since the calculation of $\langle 1/r_{ij}^3 \rangle$ for D_{17} and D_{47} involve such motional averages. Furthermore, to calculate D_{14} it is necessary to specify whether the two methyl group rotations are correlated or not.

Four types of rotational models were examined:

1. Free rotation of the methyl groups.

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2. The methyl groups executing a stochastic jump through 120°, with each one of the three protons occupying a position in the effective symmetry plane with equal probability. Here four different possibilities of "three-fold potentials" may be distinguished, namely staggered-eclipsed (see Figure 2b), eclipsed-staggered, eclipsed-eclipsed and staggered-staggered rotomers.

3. A random jump of the methyl group protons with equal weights assigned to the eclipsed-staggered and staggered-eclipsed conformers, i.e., a hindered rotation in a "correlated six-fold potential".

4. All four possible rotomers represented by case 2 occurring with equal probability, i.e., an "uncorrelated six-fold" potential.

In these "best-fit" calculations, a minimum rms error between the observed and the calculated dipolar coupling constants was obtained with the dihedral angles of $\omega = 3$ and $\varepsilon = 12$ for the "three-fold" rotation involving staggered-eclipsed rotomer. All other rotomers of the "three-fold" cases yielded rms errors outside the acceptable error limits of Dij's.

On the other hand, for either the "free-rotation" or both cases of "six-fold" rotations, minimum rms errors were obtained when the dihedral angles are $\omega = 13 \pm 1$ and $\varepsilon = 5 \pm 1$. All these calculations were performed with the fixed geometry of DMF, reported in Figure 2b.

The sensitivity of the calculation to the assumed geometry was tested by varying the two geometrical parameters suspected to contain the largest uncertainties, namely the C-N bond length and the angle $H_7\hat{C}N$, χ. Variation of the C-N length with a fixed value of $\chi = 113°$ altered the dihedral angles by less than ± 2°. However, the dihedral angle ω changed by as much as ± 10° for the "staggered-eclipsed" rotomer for a variation of the amide angle, χ through ± 7° from 113° (see Table 2).

The experimental data do not permit us to discriminate between the two significantly distinct models for methyl rotations, namely free (or "six-fold") and "three-fold" rotation. Nonetheless, irrespective of the model assumed for the mode of rotation about the N-C' and N-C" bonds, the results can be fitted to a reasonable structure of DMF only

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TABLE 2

DIHEDRAL ANGLES FROM "BEST-FIT" CALCULATIONS FOR VARIOUS ASSUMED MODELS OF METHYL ROTATION

DIHEDRAL ANGLES	1	2	3	4
(a) Fixed geometry, using data given in Fig. 2b.				
ε	3.7	11.8	5.3	3.7
ω	12.4	2.6	14.1	12.0
(b) Variation of $H_7\hat{C}N$ between 106° to 120°.				
ε	3 ∓ 1*	12 ∓ 2	5 ∓ 1	4 ∓ 2
ω	12 ± 6*	2 ± 10	14 ± 4	11 ± 6
(c) Variation of C-N bond distance.				
ε	3.5 ± 0.7**	11.7 ± 0.1	5.2 ± 0.2	3.4 ± 0.7
ω	12.2 ± 0.7**	1.6 ± 2.2	13.8 ± 1.0	11.6 ± 0.9

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1 = Free rotation; 2 = "3-fold" staggered-eclipsed rotomer shown in Figure 2b; 3 = "6-fold" correlated; 4 = "6-fold" uncorrelated

*For a variation of ± 7° in the amide angle χ, i.e., 113 ± 7°, the corresponding variations in ε and ω are indicated as deviations from their mean values. All other geometrical data are the same as given in Figure 2b.

**For a variation of 0.045 Å in the assumed C-N bond distance, i.e., 1.335 ± 0.045 Å, the corresponding variations in ε and ω are indicated as deviations from their mean values. All other geometrical data are the same as given in Figure 2b.

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if considerable nonplanar distortions are present around the nitrogen atom. Similar nonplanar distortions have been recently observed for N-methylformamide[4,5] and N-methylacetamide.[6] Further studies with C^{13} and/or ^{15}N enriched DMF seem to be warranted. The increased number of dipolar coupling constants from isotopic studies can be expected to shed more light on the problem.

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