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THE AMIDE PLANARITY AS STUDIED BY NMR OF ORIENTED MOLECULES - THE SPECTRUM OF N-METHYLACETAMIDE

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The use of the technique of NMR spectroscopy of molecules oriented in the nematic phase of liquid crystals for the study of the 'planarity' of the three bonds meeting at the nitrogen atom in a peptide unit has been suggested[1] and applied to the simplest member, namely, N-methyl formamide. Such studies are of fundamental importance since in most of the theoretical calculations, a peptide unit is assumed to be completely planar whereas the necessity of considering non-planar distortions in such a unit has been pointed out.[2] For N-methyl formamide, using reasonable values of the bond lengths and the bond angles, it was found that the results are consistent with the molecule having a plane of symmetry which may arise, either from the H.CO.NH.C moiety of the molecule being rigidly planar or from a 'rapid inversion' through the nitrogen atom. The results support the former if there is a 'free' rotation of the CH_3 group about the $N-CH_3$ bond. However, if the methyl group rotation is hindered in a 3-fold potential, the results are in better agreement with the latter. In this case the conformations for which a C-H bond of the methyl group is 'staggered' with respect to the N-H bond are more favoured; the dihedral angles $\Delta\omega$ and ν_H defined according to the standard convention[2] give the nonplanar distortions about the nitrogen atom. ω is the dihedral angle ($C_1^{\alpha}CNC_2^{\alpha}$) between the planes $C_1^{\alpha}CN$ and CNC_2^{α} (fig. 1). It is 180° for a <u>trans</u> planar unit. $\Delta\omega$ is the variation in (positive in the clockwise direction). ν_H is the dihedral angle ($C_1^{\alpha}CNH$) between the planes $C_1^{\alpha}CN$ and CNH. It is 0° for a <u>trans</u> planar unit. For N-methyl

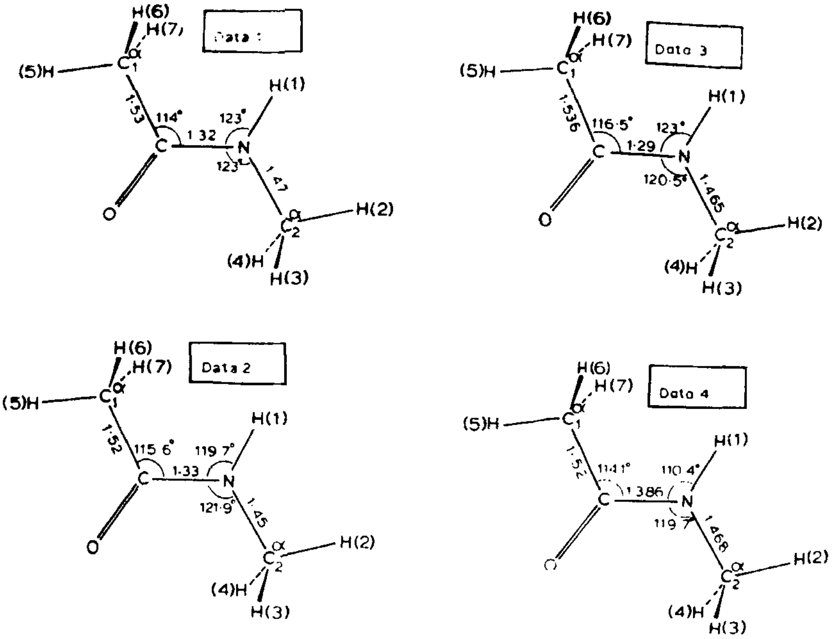

Figure 1. Bond length (in Å) and bond angle data used. The four data correspond to those reported in the literature.[6-9]

formamide, a value of nearly 10° was estimated for the dihedral angles $\Delta\omega$ and ν_H under the assumption that they are equal in magnitude but opposite in sign.[2] Furthermore, separate spectra due to the cis and the trans species could be observed and interpreted in N-methyl formamide[3] whereas in N-methyl acetamide, the spectrum due to trans species alone was observed.

In the present note, we report NMR results on the next higher member, namely, N-methyl acetamide oriented in the nematic phase of 4-methoxybenzylidene-4-amino-α-methyl cinnamic acid-n-propyl ester (A). The PMR spectrum (fig. 2) was recorded on a Bruker-360 Fourier Transform spectrometer and analysed with the help of the LAOCOONOR programme.[4]

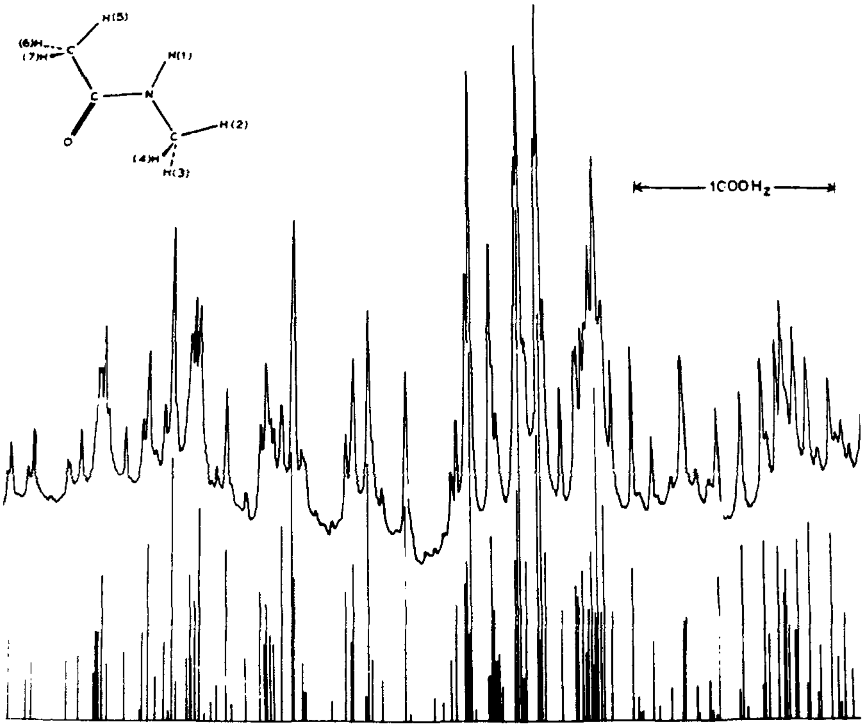

Figure 2. Observed and calculated PMR spectra of N-methyl acetamide oriented in the nematic phase of (A). Solute concentration = 9 mole %, probe temperature = 25°C, spectrometer frequency = 360 MHz.

Values of the derived dipolar couplings in Hz are: $D_{12} = -174.3$, $D_{15} = -227.5$, $D_{23} = 436.8$, $D_{25} = -48.1$ and $D_{56} = 419.5$. The indirect couplings (Hz) were determined as: $J_{12} = 4.7$, $J_{15} = -0.5$ and $J_{25} = 0.3$ and the chemical shifts (Hz) as: $\nu_2 - \nu_1 = 1598.0$ and $\nu_5 - \nu_1 = 1878.3$. Indirect couplings within the protons of the methyl groups do not influence the spectrum due to 'full equivalence'.[10] Errors of the coupling constants were estimated as 0.1 Hz and those of the chemical shifts 0.2 Hz.

The proton NMR spectrum of N-methyl acetamide provides 5 distinct HH direct couplings which have been used to study the planarity of the peptide unit in N-methyl acetamide. The procedure involves a checking of the internal consistency of the dipolar couplings assuming the known geometry and deriving the 'best fit' values of the elements of the order matrix (S) with the help of a 'least-square-fit' procedure.[5] Influences of molecular vibrations were neglected.

The bond length and the bond angle data for the peptide unit[6-9] are given in Figure 1 (data 1 to 4). Data 1 refer to the standard Pauling-Corey geometry of the peptide unit.[6] Data 2 give the average values from some recent X-ray and neutron diffraction studies on several peptides.[7] Data 3 correspond to the X-ray results on N-methyl acetamide[8] with N-H bond length equal to 1.00 Å and the ∠ CNH = 123° (Pauling-Corey values[6]). The electron diffraction values[9] which are not very accurate are given in data 4. The C-H bond length was assumed as 1.10 Å and the HCH bond angle was given the tetrahedral value (109.48°). In order to obtain an estimate of the errors due to uncertainty in the geometrical data, the computations were carried out using all the four data given in Figure 1.

If the peptide unit is rigidly planar or when there is a rapid inversion through the nitrogen atom, only 3 S-values have to be derived from the 5 HH direct dipolar couplings provided the molecular geometry and the modes of rotation of the methyl groups about the N-C_2^α and the C-C_1^α bonds are known. In view of the lack of the precise knowledge of the barrier to rotation of the methyl group in this case, the following possibilities were considered.

a) Free rotation of the methyl groups
b) Rotations of the methyl groups hindered in 3-fold potentials such that the methyl groups ($C_2^\alpha H_3^\alpha$ and $C_1^\alpha H_3^\alpha$) are 'staggered' or 'eclipsed' about the N-H or the C=O bonds respectively. The methyl groups themselves were assumed rigid and no coupled motion between the two methyl groups was considered.

The minimum r.m.s. error between the observed and the calculated dipolar couplings was obtained when the dihedral angles were 10 ± 4° depending upon the geometrical data for the peptide unit.

It may be emphasized that investigations on the isotopically enriched ^{13}C and ^{15}N species will provide more conclusive results since the system would then be well overdetermined and assumptions on the molecular geometry would not be necessary. It would also be possible to derive reliable information on the mode of rotation of the methyl groups.

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