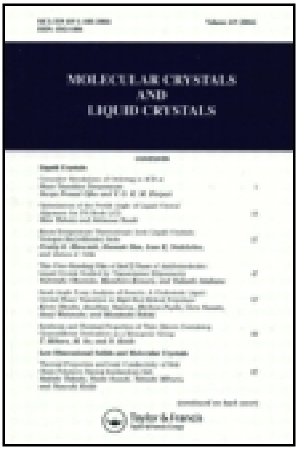


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# Nmr Spectra Of Isotopically Enriched N-Methyl Formamide In Isotropic And Nematic Media

C. L Khetrapal [a], A. C. Kunwar [b] & S. Ramaprasad [c]

[a] Raman Research Institute, Bangalore, 560006, India

[b] Department of Biophysics, University of Chicago, Chicago, Illinois, U.S.A.

[c] Indian Institute of Science, Bangalore, 5600012, India

Version of record first published: 28 Mar 2007.

To cite this article: C. L Khetrapal , A. C. Kunwar & S. Ramaprasad (1976): Nmr Spectra Of Isotopically Enriched N-Methyl Formamide In Isotropic And Nematic Media, Molecular Crystals and Liquid Crystals, 34:5, 123-126

To link to this article: http://dx.doi.org/10.1080/15421407608083899

*Mol. Cryst. Liq. Cryst.*, Vol. 34 (Letters), pp. 123-126

Printed in U.S.A.

# NMR SPECTRA OF ISOTOPICALLY ENRICHED N-METHYL FORMAMIDE IN ISOTROPIC AND NEMATIC MEDIA

C.L. KHETRAPAL,* A.C. KUNWAR** AND S. RAMAPRASAD***

*Raman Research Institute, Bangalore 560006, India

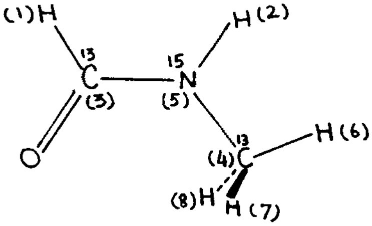
**Department of Biophysics, University of Chicago, Chicago, Illinois, U.S.A.

***Indian Institute of Science, Bangalore 560012, India

(Received: October 27, 1976)

ABSTRACT - NMR spectra of $^{15}$N-methyl ($^{13}$C) formamide ($^{13}$C) in isotropic as well as liquid crystalline nematic phases have been studied. The NMR and the structural parameters are derived.

In continuation with our work$^{1-3}$ on the study of the amide planarity, we have recently investigated the NMR spectra of $^{13}$C and $^{15}$N isotopically enriched N-methyl formamide in the isotropic as well as in a nematic phase. The spectra of the sample obtained from Merck, Sharp and Dohme of Canada indicate the presence of cis and trans $^{15}$N-methyl ($^{13}$C)-formamide ($^{13}$C), cis and trans $^{15}$N-methyl formamide ($^{13}$C) and trans $^{15}$N-methyl ($^{13}$C)-formamide with trans $^{15}$N-methyl ($^{13}$C)-formamide ($^{13}$C) (Structure 1) being present to



(Structure 1)

the major extent. The detailed analyses of the spectra were performed only for the predominant species.

The $^{13}$C and the $^{1}$H-NMR spectra in the neat liquid were recorded on the Brüker HX-90 and HX-270 NMR spectrometers respectively and analysed using the LAOCOONOR programme[4] on an IBM-370 computer. Values of the parameters are given in Table 1.

Signs of the HH and the $^{15}$NH indirect couplings ($J_{ij}$'s) in Table 1 were assumed from the earlier study of $^{15}$N-methyl formamide.[5,6] The indirect couplings between $^{13}$C and the directly bonded $^{1}$H were assumed positive. The signs of the other indirect couplings could not be determined. However, a combination of these studies with those in the nematic solvent together with the known geometry may throw some light on the signs of these coupling constants.

An analysis of the PMR spectrum at 270 MHz in the nematic phase of 4-methoxybenzylidene 4-amino-α-methyl cinnamic acid-n-propyl ester provides values of the parameters included in Table 1. During such an analysis, the signs and the magnitudes of the indirect couplings which were determined from the spectrum in the isotropic medium were used. However, since the signs of the indirect couplings $J_{14}$, $J_{23}$, $J_{24}$ and $J_{36}$ are not known, the corresponding ($J_{ij}$ + $2D_{ij}$) values (where $D_{ij}$'s are the direct dipolar couplings as defined in the LAOCOONOR programme[4]) are reported in Table 1. Since only the proton spectrum in a nematic solvent is analysed, it is difficult to label the dipolar couplings to particular heteronuclei. The values of the dipolar couplings given in the table correspond to reasonable bond lengths and bond angles in N-methyl formamide.

The direct dipolar couplings $D_{46}$, $D_{56}$ and $D_{67}$ provide the HCH bond angle and the angle which the line joining nuclei 5 and 6 makes with the bond connecting the nuclei 4 and 5 (Structure 1), irrespective of whether the three bonds meeting at the nitrogen atom lie in one plane or not. Neglecting the influence of molecular vibrations and using the standard equations,[7] these values are determined at 108.5° and 30.7°.

A preliminary interpretation of the various direct dipolar couplings indicates significant non-planar distortions around the nitrogen atom provided influences of

Table 1

Spectral parameters in trans $^{15}$N-methyl ($^{13}$C) formamide ($^{13}$C) [$J_{ij}$'s are the indirect spin-spin couplings between nuclei i and j, $D_{ij}$'s are the direct dipolar couplings and $(\nu_i - \nu_j)$ are the chemical shifts]

| $^1$H and $^{13}$C spectra in the isotropic phase | | PMR spectrum in the nematic phase | |
|---|---|---|---|
| Parameter | Value (Hz) | Parameter | Value (Hz) |
| $J_{12}$ | 1.91 | $D_{12}$ | - 346.7 |
| $J_{13}$ | 191.65 | $D_{13}$ | - 172.4 |
| $J_{14}$ | ± 5.17 | $(J_{14} + 2D_{14})$ | - 23.2 |
| $J_{15}$ | - 15.56 | $D_{15}$ | 26.2 |
| $J_{16}$ | - 0.94 | $D_{16}$ | - 31.2 |
| $J_{23}$ | ± 3.94 | $(J_{23} + 2D_{23})$ | - 248.6 |
| $J_{24}$ | ± 2.79 | $(J_{24} + 2D_{24})$ | - 32.3 |
| $J_{25}$ | - 93.46 | $D_{25}$ | 136.1 |
| $J_{26}$ | 4.83 | $D_{26}$ | - 33.1 |
| $J_{34}$ | ± 1.43 | $D_{34}$ | * |
| $J_{35}$ | ± 13.84 | $D_{35}$ | * |
| $J_{36}$ | ± 3.81 | $(J_{36} + 2D_{36})$ | - 37.2 |
| $J_{45}$ | ± 10.57 | $D_{45}$ | * |
| $J_{46}$ | 137.83 | $D_{46}$ | 77.1 |
| $J_{56}$ | 0.97 | $D_{56}$ | 9.65 |
| $J_{67}$ | Does not influence | $D_{67}$ | 112.9 |
| $\nu_2 - \nu_1$** | 14.69 | $\nu_2 - \nu_1$** | 240.4 |
| $\nu_6 - \nu_1$** | 1463.15 | $\nu_6 - \nu_1$** | 1424.4 |
| $\nu_4 - \nu_3$† | 3143 | $\nu_4 - \nu_3$ | * |

*cannot be determined from the PMR spectrum

**at 270 MHz; †at 22.63 MHz

molecular vibrations are neglected. The dihedral angles H(1)-C(3)-N-H(2) and H(1)-C(3)-N-C(4) describing the non-planar distortions around the nitrogen atom, defined according to the standard conventions[8] have been estimated to differ by 11 ± 4° from the values of 0° and 180° for a completely planar configuration.

We are grateful to Professor G.N. Ramachandran for suggesting the problem and taking keen interest in the progress of this work. Partial financial support of the National Institutes of Health (USA) under Grant No. USPHS-11493 is gratefully acknowledged.

## References

1. C.L. Khetrapal, A.C. Kunwar and K.R.K. Easwaran, Proceedings of the International Liquid Crystals Conference, Bangalore (1973), Pramana Supplement 1, p. 483.

2. S. Ramaprasad, H.P. Kellerhals, A.C. Kunwar and C.L. Khetrapal, Mol. Cryst. Liquid Cryst. Letters 34(1), 19 (1976).

3. C.L. Khetrapal, A.C. Kunwar and S. Ramaprasad, VII International Conference on Magnetic Resonance in Biological Systems, Canada (1976).

4. P. Diehl, C.L. Khetrapal and H.P. Kellerhals, Mol. Phys. 8, 567 (1964).

6. R.J. Chuck, D.G. Gillies and E.W. Randall, Mol. Phys. 16, 121 (1969).

7. P. Diehl and C.L. Khetrapal, NMR-Basic Principles and Progress (Springer-Verlag, Berlin), 1, 38 (1969).

8. G.N. Ramachandran, A.V. Lakshminarayanan and A.S. Kolaskar, Biochim. Biophys. Acta, 303, 8 (1973) and the references therein.