

The structure of and the internal rotation in N,N-dimethyl uracil

C L KHETRAPAL* and A C KUNWAR

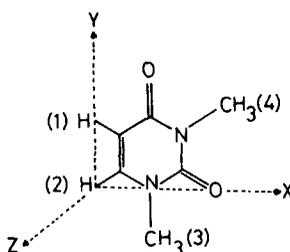
Permanent address for communication: Raman Research Institute, Bangalore 560 080, India
* National Institutes of Health, Bethesda, Maryland 20205, USA

Abstract. From the proton NMR spectra of N,N-dimethyl uracil oriented in two different nematic solvents, the internal rotation of the methyl groups about the N-C bonds is studied. It has been observed that the preferred conformation of the methyl group having one carbonyl in the vicinity is the one where a C-H bond is in the ring plane pointing towards the carbonyl group. The results are not sensitive to the mode of rotation of the other methyl group. These data are interpreted in terms of the bond polarisations.

Keywords. NMR; N,N-dimethyluracil; order parameter; oriented molecules.

1. Introduction

The use of NMR spectroscopy of oriented systems to investigate the structure and conformation of biologically important molecules has been restricted to relatively few systems (Khetrapal 1981) due to difficulties arising from low solubilities, lack of symmetry and structural complications. However, the problems can be overcome by suitable experimentation in certain cases. Using more sensitive instruments, and performing the experiments under different orientation conditions, are helpful in general. When the number of the geometrical and the order parameters (S_{ij} 's) required to be determined in a system exceeds that of the dipolar couplings (D_{ij} 's), at best only partial structural information can be derived from a single experiment. However, if the studies are undertaken in different liquid crystals, the total number of dipolar couplings available for the determination of molecular geometry may be enhanced under the assumption that the molecular geometry does not change in different solvents. In N,N-dimethyl uracil (structure 1), a single proton magnetic resonance spectrum (without



Structure 1. N,N-dimethyl uracil.

* To whom all correspondence should be addressed.

^{13}C - ^1H and ^{15}N - ^1H satellites) does not provide sufficient dipolar couplings so as to enable the relative proton positions, mode of internal rotation and the molecular order to be derived. However, if spectra in two different solvents are studied, complete geometric information can be obtained. The results are discussed in the present paper.

2. Experimental

About 8 and 6 mole per cent solutions of N,N-dimethyl uracil in N-(*p*-methoxybenzylidene)-*p'*-*n*-butylaniline (MBBA) and *p*-*n*-butyl-*p'*-methoxyazoxybenzene (Merck phase IV) were studied on Bruker WM-250 and WH-270 FT-NMR spectrometers respectively. The spectra were recorded at 24°C and 21°C for the solutions in MBBA and Merck phase IV, respectively. Two hundred and fifty scans were accumulated for the spectrum recorded on the WM-250 and Fourier transformed with the help of the ASPECT-2000 computer. For the spectrum recorded on the WH-270 spectrometer, 240 free induction decays were collected and Fourier-transformed on the BNC-12 computer. The average line-width was 5 Hz.

3. Spectral analysis

The proton magnetic resonance spectrum of N,N-dimethyl uracil recorded in chloroform (-d) provides fine structure only due to the 3-bond indirect HH coupling between nuclei *i* and *j* ($J_{ij} = J_{12}$); this coupling constant has been determined as 7.72 Hz. Other indirect proton-proton coupling constants could not be determined from the spectrum in the isotropic medium.

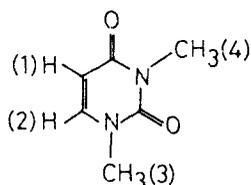
The proton spectra in the nematic solvents were analysed with the help of the LEQUOR (Diehl 1971b) program on a DEC-1090 computer. The chemical shifts ($\nu_i - \nu_j$), the direct (D_{ij}) and the indirect (J_{ij}) spin-spin couplings could all be determined iteratively from the observed spectra. The number of lines assigned for the spectrum in MBBA was 243 and that in the Merck phase IV was 261. The root-mean-square (RMS) errors of the fit were 0.65 and 1.09 Hz respectively.

The spectral parameters thus determined are given in table 1. Errors of the parameters (table 1) correspond to those given by the LEQUOR program.

4. Results and discussion

Values of the indirect spin-spin coupling constant (J_{12}) obtained from the spectra in the isotropic and nematic phases agree with each other. The long-range indirect spin-spin couplings which could not be determined from the spectrum in the isotropic medium have been obtained from the nematic phase spectra. Signs and magnitudes of the various long-range indirect spin-spin couplings determined from the spectra in MBBA and Merck phase IV agree with each other, indicating negligible solvent effects.

Each spectrum in the nematic phase provides 8 direct dipolar couplings. For the situations when (i) the axes of methyl group rotations are along the respective N-CH₃ bonds, (ii) the methyl groups themselves are rigid, (iii) the influences of molecular vibrations are neglected, (iv) r_{12} is used as the scaling distances (2.30 Å) (Banerjee *et al* 1977), (v) the molecule has a plane of symmetry, and (vi) the motions of the two methyl

Table 1. Spectral parameters for *N,N*-dimethyluracil oriented in nematic solvents.

Parameter	Value (Hz)	
	In MBBA at 250 MHz	In Merck phase IV at 270 MHz
$\nu_1-\nu_4$	-467.37 ± 0.13	-466.86 ± 0.22
$\nu_2-\nu_4$	-761.24 ± 0.13	-832.80 ± 0.22
$\nu_3-\nu_4$	94.37 ± 0.07	99.05 ± 0.08
J_{12}	7.83 ± 0.14	7.70 ± 0.20
J_{13}	-0.26 ± 0.09	-0.13 ± 0.16
J_{14}	0.30 ± 0.21	0.02 ± 0.21
J_{23}	0.03 ± 0.10	-0.13 ± 0.15
J_{24}	-0.23 ± 0.14	-0.52 ± 0.15
J_{34}	0.11 ± 0.05	0.03 ± 0.07
D_{12}	-1270.34 ± 0.07	-1859.88 ± 0.10
D_{13}	-126.61 ± 0.06	-178.49 ± 0.09
D_{14}	-2.90 ± 0.11	-11.74 ± 0.11
D_{23}	-473.72 ± 0.08	-651.74 ± 0.11
D_{24}	-27.82 ± 0.08	-49.94 ± 0.08
D_{34}	-81.10 ± 0.03	-126.92 ± 0.04
D_{33}^*	1672.24 ± 0.03	2459.03 ± 0.04
D_{44}^*	429.02 ± 0.03	779.87 ± 0.04

* Direct dipolar couplings within the respective methyl protons.

groups are not correlated, 8 geometrical parameters define the proton positions for a particular mode of rotation of the methyl groups. The number of order parameters (S_{ij} values) to be determined for each experiment is 3. The 8 geometrical and 3 order parameters cannot be determined from a single experiment. If, however, the experiments are performed in two different liquid crystals, a total number of 6 orientational and 8 geometrical parameters have to be determined from the observed 16 direct dipolar couplings. The inherent assumption in such investigations is that the molecular structure is not solvent-dependent. By appropriate modification of the iterative computer program SHAPE (Diehl *et al* 1971a) the best fit geometrical and the orientational parameters can be determined. With the right-handed Cartesian coordinate system for which the origin is at proton position 2 and the positive y -axis lies along the axis joining proton 2 to 1 with the xy plane being the molecular plane of symmetry, the following parameters (given in table 2 along with the x -ray crystallographic data, Banerjee *et al* 1977) were determined by the modified version of the SHAPE program on a DEC-1090 computer:

- (i) The angle α_1 between the y -axis and the N-CH₃ bond axis of the CH₃ group marked (3) in structure 1.

Table 2. Geometrical and order parameters in N,N-dimethyluracil.

Parameter	Mode of rotation of methyl groups				X-ray values*
	E3,E4	E3,S4	E3,P4	E3,F4	
α_1 (degrees)	2.7	2.7	2.7	2.7	1.4
α_2 (degrees)	25.5	24.4	25.0	25.0	26.2
X_3 (Å)	1.88	1.82	1.85	1.85	1.95
Y_3 (Å)	-1.85	-1.83	-1.84	-1.84	-1.95
X_4 (Å)	4.78	4.84	4.81	4.81	4.76
Y_4 (Å)	2.50	2.44	2.47	2.47	2.48
$(r_{\text{HH}})_3$ (Å)	1.77	1.77	1.77	1.77	
$(r_{\text{HH}})_4$ (Å)	1.82	1.82	1.82	1.82	
S_{xx}	0.0014	-0.0008	0.0003	0.0003	
S_{yy}	0.1287	0.1287	0.1287	0.1287	
S_{xy}	0.0143	0.0199	0.0171	0.0171	
S'_{xx}	0.0093	0.0065	0.0078	0.0078	
S'_{yy}	0.1885	0.1885	0.1885	0.1885	
S'_{xy}	0.0298	0.0377	0.0337	0.0337	
RMS error (Hz)	0.08	0.10	0.09	0.09	

* Based on an average value of the methyl C-H distance and the tetrahedral value for the methyl HCH bond angles.

- (ii) The angle α_2 between the x-axis and the N-CH₃ axis of the CH₃ group marked (4) in structure 1.
- (iii) The (x,y) coordinates of the centres of the two equilateral triangles formed by each of the methyl group protons. They are referred as (X_3 , Y_3) and (X_4 , Y_4) respectively for the methyl group designated as (3) and (4) in structure 1.
- (iv) The HH distance within the methyl groups. They are referred as $(r_{\text{HH}})_3$ and $(r_{\text{HH}})_4$ for the methyl groups (3) and (4) respectively.
- (v) Two sets of order parameters referred as S_{xx} , S_{yy} , S_{xy} and S'_{xx} , S'_{yy} , S'_{xy} for the experiments in MBBA and Merck phase IV respectively.

To determine the above parameters, the following modes of methyl group rotations were considered: For the methyl group (3) (a) a free rotation (designated as F3 in table 2) about the N-C bond, (b) 3 energetically equivalent conformers each with a C-H bond of the methyl group pointing towards or away from the adjacent C=O group (referred to as E3 or S3 respectively), (c) 3 equivalent conformers each with a C-H bond of the methyl group perpendicular to the molecular plane of symmetry (designated as P3) were considered. Similar possibilities of the mode of rotation of the methyl group (4) were also considered and they are designated as F4, E4, S4 and P4 respectively in table 2. In this case E4 means that one C-H bond of the methyl group (4) points towards the carbonyl bond adjacent to the methyl group (3). All the combinations of the various possibilities were taken into account. The RMS error between the observed and the best-fit-calculated dipolar couplings was determined. It was found that the RMS error is larger than 0.6 Hz for all P3 possibilities. The magnitude of this error is nearly 8 times larger than that for some other possibilities considered and

hence this is not acceptable. The results, therefore, indicate that the conformation with a C-H bond of the methyl group (3) being perpendicular to the ring plane is not favoured. In table 2, therefore, the possibilities with P3 are not included. For the S(3) possibilities, the RMS error is fairly large (0.14–0.15 Hz). In addition, the geometrical parameters are in complete disagreement with those obtained for x-ray data. Deviations up to 0.4 Å have been observed in some of the geometrical parameters. Hence, such conformers are also considered less favoured. Such results are also not included in table 2. The F3 possibilities provided small RMS errors (0.10 Hz) but the derived geometrical parameters were in drastic disagreement with those obtained from the x-ray crystallographic data. Deviations up to 0.23 Å were observed in some of the geometrical parameters thus determined and their values obtained from x-ray crystallographic data. Consequently, the free rotation of the methyl group (3) is ruled out.

The minimum RMS error (0.08–0.10 Hz) is obtained for the E3 possibilities irrespective of the mode of rotation of the methyl group (4). The results, therefore, indicate that the preferred conformation of *N,N*-dimethyl uracil in the liquid phase is the one where one C-H bond of the methyl group (3) points towards the adjacent C=O group. The results are not very sensitive to the mode of rotation of the methyl group (4). The geometrical data derived from the NMR and the x-ray experiments are in reasonable agreement with each other.

The results can be explained in terms of the polarisations of the various bonds as suggested earlier in connection with the studies on phenyl silane (Khetrapal and Becker 1981). The C-H and the C=O bonds have opposite polarisations ($C^{\delta-}-H^{\delta+}$ and $C^{\delta+}-O^{\delta-}$) and hence, due to electrostatic attraction, the conformer with a C-H bond of the methyl group (3) pointing towards the adjacent C=O group is preferred. On the other hand, for the methyl group (4), the presence of the C=O groups on either side at almost equal distances makes it hard either for the E4 or the S4 conformer to be preferred. The results are not very sensitive to the mode of rotation of the methyl group (4). The experimental results are, therefore, consistent with the bond polarisation hypothesis for the preferred conformation of *N,N*-dimethyl uracil.

5. Conclusion

The preferred conformation of the *N,N*-dimethyl uracil determined from NMR studies in nematic solvents corresponds to the one where a C-H bond of the methyl group (3) points towards the adjacent C=O group. The results are not sensitive to the mode of rotation of the methyl group (4). They have been explained in terms of the bond polarisation hypothesis reported earlier (Khetrapal and Becker 1981).

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