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NMR Spectra of molecules oriented in a lyotropic mesophase Part I : The spectra of pyridazine, pyrimidine and pyrazine†

C L KHETRAPAL*, A C KUNWAR* and A V PATANKAR**
*Raman Research Institute, Bangalore 560006, India
**Bhabha Atomic Research Centre, Bombay 400085, India

Abstract. A lyotropic mesophase formed by a 14 : 1 : 1 : 20 mixture (by weight) of sodium dodecyl sulphate, sodium sulphate, decanol and heavy water is used to study the PMR spectra of pyridazine, pyrimidine and pyrazine. Since the ordering of the molecules is much lower in this case compared to that in a thermotropic mesophase, analysis of the spectra was considerably simplified. Some of the dipolar couplings could be guessed fairly accurately even from the first order analysis. The geometry information and the order parameters are derived in each case. Ratios of interproton distances thus determined are compared with those obtained from the studies in the thermotropic mesophase. For pyrimidine and pyrazine they are found to agree. However, in pyridazine a deviation of about 5% in one of the distance ratios is observed. This may be attributed to a hydrogen bonded complex formed between pyridazine and water in the lyotrophic phase. In pyridazine, the S-value along the C_2 axis of symmetry is found positive and that perpendicular to the plane of the ring negative as in thermotropics. The order parameter in the ring plane along an axis perpendicular to the symmetry axis has the largest positive value. In pyrimidine, the S-value of the axis perpendicular to the plane of the ring is negative and its magnitude decreases with the increase of temperature such that at 45°C it is nearly zero. The order parameter of the symmetry axis has the largest positive value.

For pyrazine it was possible to determine the signs of the order parameters in this phase by assuming the signs of the indirect spin–spin couplings. This was not possible in thermotropic liquid crystal solvents. The S-value of an axis perpendicular to the ring plane was found positive as for most of the aromatics in a lyotropic mesophase.

1. Introduction

The use of a lyotropic mesophase formed by a mixture of C_8 or C_{10} alkyl sodium sulphate, the corresponding alcohol, sodium sulphate and water (or heavy water) in approximate ratios of 8 : 1 : 1 : 10 has earlier been suggested as the orienting medium in NMR experiments[1-3]. Studies in a lyotropic phase aimed at the elucidation of molecular structure are relatively rare

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compared to those in a thermotropic mesophase. This is probably due to the fact that the orientation processes in the former are much slower and are rather critically dependent on the concentration and the purity of the ingredients. On the other hand such a phase complements a thermotropic mesophase in that some of the substances which are not soluble in the latter may dissolve in the former. Further, such a phase permits the spinning of the sample without destroying the orientation in commonly available magnetic fields where the direction of the field and the axis of the sample spinning are perpendicular to each other. This results in relatively sharp lines (with widths $\simeq$ 1–2 Hz). Another feature of such a phase is the relatively low molecular order of the dissolved species which sometimes (1) simplifies the spectra such that it may be possible to estimate the NMR parameters from the first order analysis to a reasonable accuracy, and (2) makes it possible to derive the information which is lost as a result of the dominating nature of the dipolar couplings. Studies on such a phase coupled with those in a thermotropic mesophase may permit the determination of the components of the chemical shift tensor in systems with C_{2v}–symmetry.

In the present paper, we report the results obtained from the PMR spectra of the title compounds dissolved in a phase (referred to as II hereafter) formed by a 14 : 1 : 1 : 20 mixture (by weight) of sodium dodecyl sulphate, decanol, sodium sulphate and deuterium oxide. The phase proposed earlier[1-3] (referred to as I hereafter) differs from II in having sodium decyl sulphate instead of sodium dodecyl sulphate in addition to somewhat different relative proportions of the ingredients.

2. Experimental

About 2% (by weight) of the solute was added to the phase and the mixture was centrifuged for about half an hour. The solutions thus prepared were transferred to the 5 mm NMR sample tubes and kept for spinning in the magnetic field for several hours ($\simeq$ 7) before the spectra were finally recorded on a Varian A–60 NMR spectrometer. The line–width varied from 1–2 Hz. The sweep time and the sweep width used were 5000s and 500 Hz respectively. Spectra of pyrimidine and pyrazine were recorded at 45 °C whereas pyridazine was studied at 35 °C. In addition, pyrimidine was also studied at 35 °C for comparison of the various results.

The statistical error in the measurements of line positions was 0.2 Hz.

3. Results and discussion

3.1. *Analysis of the spectra*

Spectra of pyridazine, pyrimidine and pyrazine are shown in figures 1–3 respectively. Since the spectrum of pyrazine is symmetrical about the centre, only the upper–field half of the spectrum is shown in figure 3.

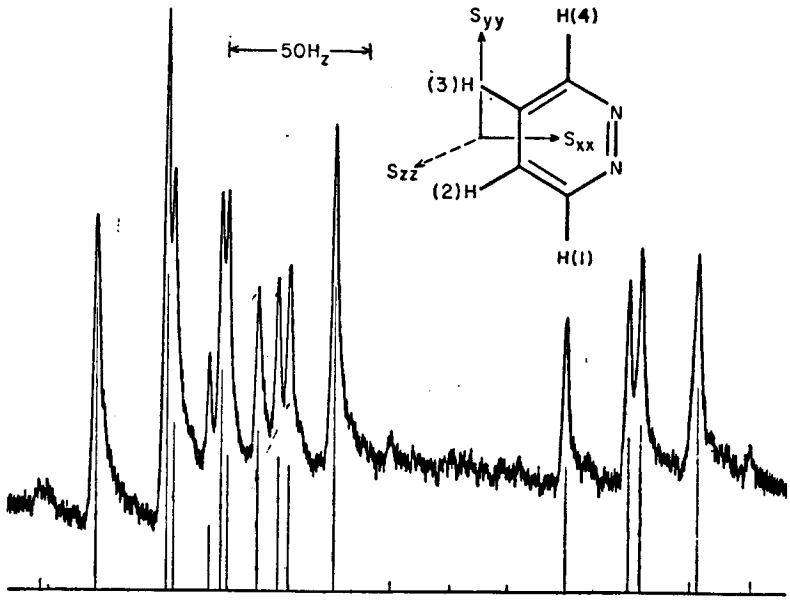


Figure 1 Observed and calculated PMR spectra of pyridazine oriented in the lyotropic phase (II). Spectrometer: A 60. Concentration: 2% (by weight). Temperature: 35° C.

In pyridazine and pyrimidine, since the chemical shifts between the various protons are relatively large compared to the direct dipolar couplings, it was possible to assign some of the groups of lines to particular protons and hence some of the parameters could be guessed fairly accurately from the first order analysis, e.g., for pyridazine (figure 1), the highest field quartet forms about half of the spectrum due to protons 2 and 3 and for pyrimidine (figure 2), the doublet of quartets at the highest field arises due to proton 3.

In pyrazine (figure 3), the spectrum consists of a symmetrical doublet of sextets[4]. In each sextet four lines are independent of the isotropic spin–spin couplings and are in the intensity ratio of 1 : 1 : 1 : 2. The remaining two lines with a total relative intensity of 3 are split up by the isotropic couplings in an approximate intensity ratio of 1 : 2; they usually overlap[5,6] in the spectra in thermotropic liquid crystals. On the other hand the separation between these two lines provides approximately $\frac{3}{2}(J_{23} + J_{13})$. The sign of this quantity relative to that of the direct couplings can be derived from the analysis. Information on the molecular orientation can thus be obtained.

The final analysis was carried out with the help of the LAOCOONOR programme[7] which also contains the definitions of the coupling constants and the chemical shifts ($\nu_i - \nu_j$). In the analysis, the chemical shifts and

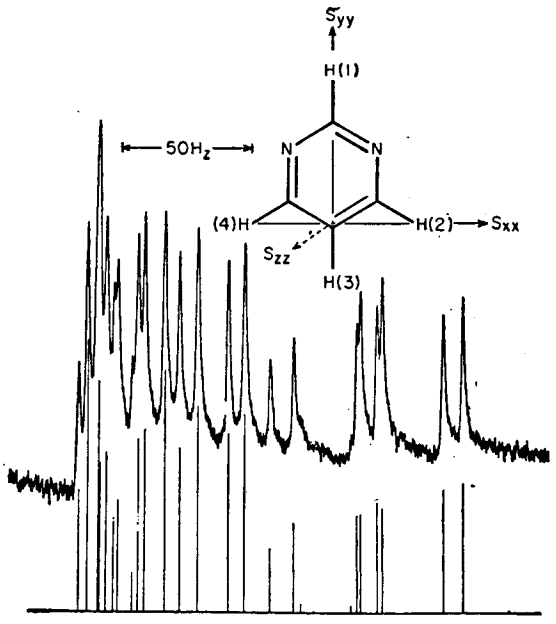


Figure 2 Observed and calculated PMR spectra of pyrimidine oriented in the lyotropic mesophase (II). Spectrometer : A 60. Concentration : 2% (by weight). Temperature : 45°C.

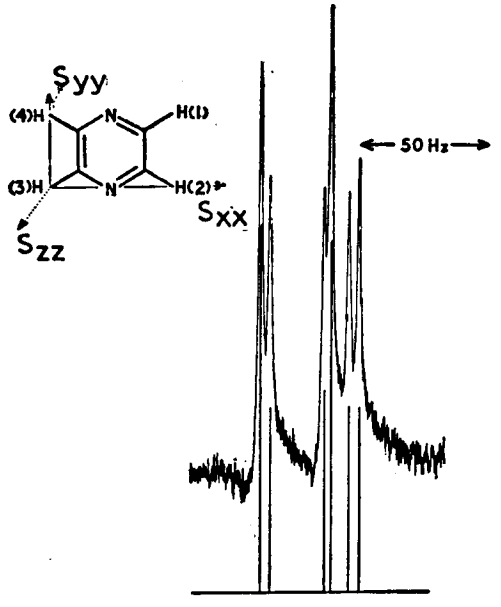


Figure 3 Observed and calculated PMR spectra of pyrazine oriented in the lyotropic mesophase (II). Only upper-field half of the symmetrical spectrum is shown. The highest field line is 174.6 Hz from the spectral centre. Spectrometer : A 60. Concentration : 2% (by weight). Temperature : 45° C.

the direct dipolar coupling constants were iterated upon and the values of the indirect couplings used were taken from the literature on the spectra in the isotropic media[8,9]. The calculations were carried out on a CDC–3600 computer. The root mean square error between the observed and the calculated line positions was 0.24 Hz, 0.26 Hz and 0.08 Hz for pyridazine, pyrimidine and pyrazine respectively. The maximum error of any line position from its experimental value was found to be 0.46 Hz for pyridazine, 0.50 Hz for pyrimidine and 0.08 Hz for pyrazine. Values of the parameters thus obtained are given in table 1.

The signs of the direct dipolar couplings were found as given in table 1 on the valid assumption that the signs of the major indirect spin–spin couplings in these cases are positive.

By carrying out iterations on the indirect coupling constants in addition to the direct ones and the chemical shifts, it was found that the direct couplings and the chemical shifts do not change beyond their experimental errors given in table 1. It was also found that (1) in pyridazine, $J_{12}=5.31$ Hz, $J_{13}=1.79$ Hz and the other couplings could not be determined with any reasonable precision, (2) in pyrimidine, it was not possible to obtain any of the indirect couplings accurately, and (3) in pyrazine, it was possible only to estimate the value of $(J_{13}+J_{14})$ as 1.6 ± 0.2 Hz. This sum is expected to have a positive sign by analogy with substituted benzenes and hence the signs of the direct couplings are as given in table 1. This information could not be derived from the spectrum of pyrazine in a thermotropic mesophase because of the overlap of the lines which are dependent upon the indirect spin–spin coupling constants[4].

3.2. *Molecular geometry*

The relations between the direct dipolar couplings and the ratios of the interproton distances reported in the literature[4,11] were used to obtain the geometry information reported in table 2. The values within parentheses are those obtained from the study in the thermotropic mesophase. The errors of the distance ratios given in table 2 correspond to those derived by changing the dipolar couplings by the amount of their deviations (table 1) such that maximum deviations in these ratios from their mean values were obtained.

Table 2 indicates that the agreement between the distance ratios obtained in the lyotropic and the thermotropic mesophases is astisfactory for pyrimidine and pyrazine. However, there are significant deviations between the values for pyridazine. We have also made an investigation on pyridazine dissolved in the lyotropic mesophase (I)[1]. We find $r_{12}/r_{23}=0.951$, $r_{13}/r_{23}=1.673$ and $r_{14}/r_{23}=1.894$ in agreement with the values obtained in the lyotropic mesophase (II). An investigation on pyridazine dissolved in 4–ethoxybenzylidene–4–*n*–butylaniline was also made. The distance ratios obtained in this phase are in agreement with those

Table 1 Spectral parameters in pyridazine, pyrimidine and pyrazine oriented in lyotropic mesophase (II). Numbering of protons refers to figures 1, 2 and 3.

Pyridazine		Pyrimidine		Pyrazine	
Parameter	Value (Hz)	Parameter	Value (Hz)	Parameter	Value (Hz)
D_{12} (= D_{34})	− 16.49 ± 0.09	D_{12} (= D_{14})	− 3.44 ± 0.05	D_{12} (= D_{34})	103.72 ± 0.03
D_{13} (= D_{24})	− 7.41 ± 0.11	D_{13}	− 4.70 ± 0.05	D_{13} (= D_{24})	− 1.28 ± 0.03
D_{14}	− 6.39 ± 0.05	D_{23} (= D_{34})	13.96 ± 0.04	D_{14} (= D_{23})	− 11.35 ± 0.03
D_{23}	− 44.38 ± 0.07	D_{24}	6.53 ± 0.05		
$\nu_2 - \nu_1$	88.58 ± 0.10	$\nu_1 - \nu_2$	− 23.53 ± 0.17		
		$\nu_3 - \nu_2$	75.65 ± 0.08		

Table 2 Distance ratios for pyridazine, pyrimidine and pyrazine as determined from the present investigations. The numbering refers to the figures 1, 2 and 3.

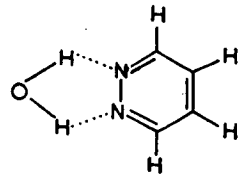
Distance ratio	Pyridazine τ	Pyrimidine τ	Pyrazine
r_{12}/r_{23}	0.943 ± 0.014	1.611 ± 0.018 μ	0.607 ± 0.002
	(0.988 ± 0.010) φ	(1.62 ± 0.01) *	(0.602 ± 0.008) †
r_{13}/r_{23}	1.673 ± 0.010	1.898 ± 0.017 μ	1.170
	(1.693 ± 0.007) φ	(1.90 ± 0.02) *	
r_{14}/r_{23}	1.908 ± 0.006	1.611	1.000
	(1.890 ± 0.004) φ		
r_{24}/r_{23}	1.673	1.697 ± 0.004 μ	1.170
		(1.706 ± 0.004)	

φ ref. 10; * ref. 11; † ref. 4. Values obtained from thermotropic mesophase.

τ Values of the distance ratios obtained from the phase (I) are: $r_{12}/r_{23} = 0.951$; $r_{13}/r_{23} = 1.673$; for pyridazine and 1.611 and 1.896 respectively for pyrimidine.

μ Values at 45° *C*; those at 35° *C* are 1.629, 1.915 and 1.701 respectively. The two agree with each other within experimental error.

obtained earlier in the thermotropic mesophase[10]. Thus the distance ratio r_{12}/r_{23} in the lyotropic mesophase is about 5% shorter than in the thermotropic phase. It may arise from a specific molecular interaction of pyridazine with either the thermotropic or the lyotropic mesophase with the result that the structure determined in that phase does not truly represent that of the pyridazine molecule. Earlier, from spectroscopic studies [12,13], a hydrogen bonded interaction of the type



involving the non-bonding electrons of nitrogen has been postulated between pyridazine and water. These sudies, therefore, provide a method to study some of the weak molecular interactions specially where the atoms directly involved in the interaction cannot be used as the probes.

For pyrimidine, exactly the same distance ratios in the two lyotropic phases were obtained (table 2) even though the molecular orientations are quite different.

3.3. *Molecular Order*

The lyotropic mesophase orients differently in the magnetic field compared to the thermotropic one in that it permits spinning of the sample about its axis in a direction perpendicular to the magnetic field without destruction of the orientation. For comparing the S-values under similar conditions of concentration and temperature, measurements in pyrimidine were carried out at two different temperatures, namely 45°C and 35°C. The results are summarized in table 3.

Table 3 shows that the magnitude of the S-values is in general larger in the phase (I) than in (II). The S_{zz} value is more negative in pyridazine than in pyrimidine at the same temperature (35 °C). At higher temperature ($\simeq$ 45 °C), the S_{zz} value in pyrimidine becomes almost zero. At 45 °C the S_{zz} value in pyrazine is positive. In pyridazine and pyrimidine, the largest S-values are found along the largest molecular axes. This behaviour is similar to what is observed for these molecules in thermotropic liquid crystals[10,11]. It should be pointed out that in pyridazine the values of the order parameters reported in table 3 might have been modified due to the formation of the hydrogen bonded complex discussed in

Table 3 *S*-values in Pyridazine, Pyrimidine and Pyrazine in the lyotropic mesophase (II) at the same concentrations. The indexing of the *S*-values refers to the coordinate systems in figures 1, 2 and 3.

S-value	Pyridazine * 35° C	Pyrimidine † 35° C	Pyrimidine † 45°C	Pyrazine ‡ 45° C
S_{xx}	0.00059 ± 0.00014	— 0.00516 ± 0.00005	— 0.00425 ± 0.00004	0.00738 ± 0.00002
	(0.0005) φ		(— 0.00651) φ	
S_{yy}	0.00564 ± 0.00001	0.00537 ± 0.00009	0.00428 ± 0.00007	— 0.01509 ± 0.00011
	(0.0079) φ		(0.00526) φ	
S_{zz}	— 0.00623	— 0.00021	— 0.00003	0.00771
	(— 0.0084) φ		(0.00125) φ	

φ Values in the phase (I)

* $r_{23} = 2.481$ Å (assumed); † $r_{24} = 4.274$ Å (assumed); ‡ $r_{23} = 4.274$ Å (assumed) 1 Å = 10^{-10} m.

section 3.2 and they need not correspond to the true values for the uncomplexed molecule. For pyrazine, the signs of the order parameters could not be obtained in thermotropics[4] and hence no such comparison could be made.

Recently, we came across the following papers by Long *et al*:

(A) *Mol. Cryst. Liquid Cryst.* **21**, 299 (1973) and **32**, 137 (1973)

(B) *Proc. Am. Chem. Soc. meeting* edited by J F Johnson and R S Porter (Plenum Press) p. 147 (1974)

Results on pyrazine, pyrimidine and pyridazine in the lyotropic phase (I) are reported in paper (A) and in the paper (B), those in a new lyotropic phase formed by potassium laurate, decanol, potassium chloride and D_2O are given.

Our results agree with those given in papers (A) and (B) for pyrazine; however, deviations outside the reported experimental errors are noticeable within references (A) and (B).

For pyrimidine in phase (I), the results are not consistent within the two references in (A). Besides in paper (A), the authors iterate upon J_{24} also and derive a value equal to $5{\cdot}3 \pm 0{\cdot}4$ Hz at 311 K and 7·6 Hz at 305 K for it. This is actually consistent with our finding that this J–value cannot be determined to any reasonable precision from such measurements. Our results on the molecular geometry of pyrimidine in phase (I) are nearly in agreement with those reported in reference (B).

In pyridazine, our results in the phase (II) do not agree with those given in references (A). However, the distance ratios determined in phase (I) from the present measurements and those derived from the data reported by Long *et al* (A) at 309 K are not in too bad an agreement. In pyridazine again, Long *et al* find that J_{12} varies from $5{\cdot}0 \pm 0{\cdot}2$ Hz at 305 K to $6{\cdot}4 \pm 0{\cdot}6$ Hz at 314 K which is too large a variation. Such a procedure in fact increases uncertainties in the determination of *D*–values.

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DISCUSSION

Dhingra : In pyridazine–water complex, how do you rule out the possibility of a 1 : 2 complex ?

Khetrapal : Firstly, as I stated earlier, our results cannot predict whether it is 1 : 1 complex or 1 : 2 complex or whether at all the hydrogen bonds are formed. The differences in the structural parameters observed in the lyotropic and the thermotropic phases are indicative of the fact that there are solvent–solute interactions either in the thermotropic or in the lyotropic phase. A survey of the literature on pyridazine–water systems leads us to believe the formation of the complexes of the type mentioned. Secondly, in the case of a 1 : 2 type of complex, I would have expected deviations in the structural parameters for all the compounds studied.