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Orientation and Structure of Pyrazine, Pyrimidine, and Pyridazine in a Lyotropic Liquid Crystal†

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Abstract—High resolution proton magnetic resonance spectra of pyrazine, pyrimidine, and pyridazine partially oriented in a lyotropic mesophase have been obtained and analyzed. The distance ratios calculated from the direct dipole-dipole couplings are compared with those reported for microwave and X-ray studies in the gaseous and solid state as well as those determined from NMR investigations of the above solutes in thermotropic nematic phases.

The average orientation of the diazines in the oriented lyotropic phase is such that the applied magnetic field is parallel to the molecular plane. In contrast, the average orientation of benzene, furan, thiophene, *p*-dithiin, and tetrafluoro-1,3-dithietane is such that the molecular ring is on the average perpendicular to the applied magnetic field. Sine benzene, furan, thiophene, and the diazines orient with the molecular plane parallel to the magnetic field in thermotropic nematic phases, contributions from different orienting factors appear to be operative in the lyotropic phase.

1. Introduction

In previous investigations involving the lyotropic liquid crystal phase reported by Flautt and Lawson,[1] we have been interested in the orientation and structure of ring systems containing heteroatoms. Earlier studies of cyclic molecules in this particular lyotropic medium by this group as well as those of other laboratories have included benzene,[2] tetrafluoro-1,3-dithietane,[3] *p*-dithiin,[4] furan[5] and thiophene.[5,6] All of the compounds above have a limited solubility in water. The degree of orientation observed for benzene, considered to be hydrophobic, dissolved in thermotropic solvents[7] and in this

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medium[2] is similar in absolute magnitude. The degree of orientation observed in the lyotropic phase for molecules such as acetone and dimethyl sulfoxide is considerably less as determined from the magnitude of the direct dipole-dipole couplings.[8] Apparently molecules soluble in aqueous media are oriented to a lesser degree than those preferring a hydrocarbon environment. An appropriate test of the above hypothesis can be based upon the study of water soluble molecules whose molecular shape is as similar as possible to the previously investigated planar systems. The diazine series, pyrazine, pyrimidine and pyridazine, possess the required properties, mentioned above. Previous structural investigations for these molecules include an NMR determination of proton–proton distance ratios for pyrazine,[9] pyrimidine,[10] and pyridazine[11] in thermotropic liquid crystal solvents as well as X-ray studies in the solid state.[12,13] In earlier microwave investigations of pyridazine, several assumptions were necessary in order to locate the protons.[14] The distance ratios given here for the diazines are the first available for this series obtained in a partially ordered aqueous environment. Comparison of structural parameters with those determined from other methods is of obvious interest.

2. Experimental

Pyrazine, pyrimidine, and pyridazine were obtained from Aldrich Chemical Co. and used without further purification. The NMR spectra of the above in aqueous solution revealed no obvious impurities. The composition by weight of the various components in the lyotropic mesophase were 40% decyl sulfate, 5% decyl alcohol, 5% sodium sulfate, and 50% deuterium oxide as described previously.[1]

The spectra were acquired on an A-60A and a Bruker HFX-90 NMR spectrometer. Each spectrum was acquired in a single scan and calibrated by the usual techniques. When an internal lock was necessary, TMS was employed in an external capillary arrangement as described in a previous paper.[3]

For pyrazine the data represent the average of 5 forward and 5 reverse scans obtained at 60 MHz. Each spectrum was analyzed separately and the spectral parameters were averaged to give final

values and standard deviations. The distance ratios were determined from the parameters of each spectrum and were averaged in a similar manner. The concentration of pyrazine was 1.02% by weight in the lyotropic liquid crystal of the composition as described above. The probe temperature was 311 °K ± 1 °K.

Data on pyrimidine represent the average of 11 scans on the A-60A at 311 °K; 8 scans acquired on the HFX-90 instrument at 90 MHz at 293.2 °K; and one scan each at 305.0 °K and 314.7 °K. Each spectrum was analyzed and the spectral parameters and distance ratios were averaged to yield final values and standard deviations. The concentration of pyrimidine was 1.16% by weight in the lyotropic liquid crystal.

Pyridazine spectra were acquired at 90 MHz. The data represent the average of 6 scans at 293.5 °K, 2 scans at 305.0 °K, 4 scans at 308.8 °K, and 2 scans at 313.7 °K. The distance ratios calculated represent the average values over the above temperature range. The concentration of pyridazine was 0.68% by weight in the lyotropic liquid crystal.

In the above temperature studies the samples were allowed to equilibrate at the desired temperature for at least 45 min.

3. Analysis

The experimental spectrum of pyrazine, Fig. 1, consists of a large doublet separation with smaller splittings observed in the upfield

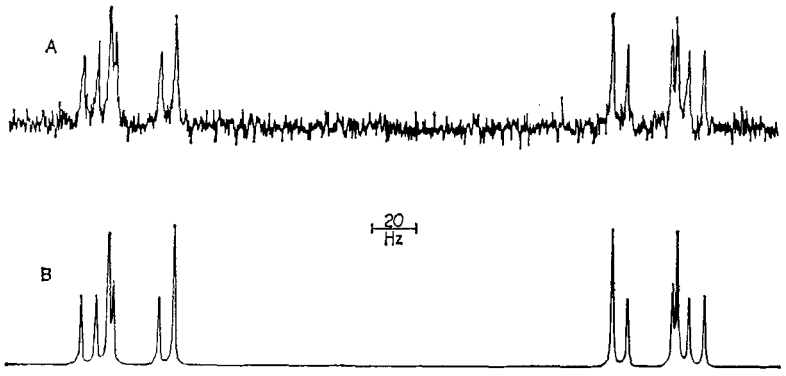


Figure 1. Experimental (A) and calculated (B) spectrum of pyrazine partially oriented in the lyotropic mesophase.

and downfield patterns. Two intense lines occur in each half of the pattern. For the purpose of discussion the lines are labeled T_1 thru T_6 starting from the innermost transition in the pattern outward. The protons in pyrazine are labeled clockwise starting α to the nitrogen in the order 1, 2, 3, and 4 with the 1,2 interaction being the ortho coupling. Two sets of constant splittings were observed $|T_1 - T_2|$, $|T_5 - T_6|$ and $|T_1 - T_5|$, $|T_2 - T_6|$. Initial values of D_{14} and D_{13} were calculated from the above set of splittings, since $D_{14} = 2/3\,|T_1 - T_5|$ and $D_{13} = 2/3\,|T_1 - T_2|$.[15] It was initially assumed that D_{13} was the smaller coupling since it involves the longest distance between protons. Therefore, the larger splitting was originally assigned to D_{14}; the smaller to D_{13}. The frequency difference between the center of the total spectrum and a point centered between $T_{1,2}$ and $T_{5,6}$ is $\cong 3/4\,|D_{12}|$.[15] The relative signs of the set determine the intensity sequence for T_1, T_2, T_5, and T_6. The absolute magnitudes of the D_{ij} determined above were combined with the three indirect couplings estimated from the values determined for pyridine.[16] This initial set was employed with various sign combinations and calculations performed until an acceptable visual simulation obtained. Changes in the ortho coupling, J_{12}, had no effect on the spectrum. Therefore, J_{12} could not be determined. The spectrum depends on the other coupling values as the sum, $J_{13} + J_{14}$. J_{14} was set equal to 0.0 and J_{13} allowed to vary in the final least squares iterations. The parameters which give an acceptable solution are given in Table 1.

TABLE 1 Spin-Hamiltonian Parameters for Pyrazine at 311 °K

$\delta(w_1 - w_2)$	0.0
J_{12}	5.00[a]
J_{13}	1.18
J_{14}	0.00[b]
D_{12}	$+152.18 \pm 0.17$
D_{13}	-4.30 ± 0.05
D_{14}	-21.79 ± 0.09
$C_{3z^2-r^2}$	+0.00730[c]
$C_{x^2-y^2}$	−0.01948

[a] The value used for J_{12} had no effect on the calculated spectrum. Units are in Hz for J_{ij} and D_{ij}.

[b] Held fixed during final iterations.

[c] Motional constants were calculated with $r_{12} = 2.4375$ Å. This value was calculated from r_{cc} of 1.378 Å, r_{C-H} of 1.05 Å and a CC − H of 120.3°.[21] The molecule-fixed axis system is given in Fig. 4.

The signs in Table 1 for the D_{ij} values are based on a positive value of J_{13}. Reversal of the signs of D_{ij} relative to J_{13} exchanges the intensities of transitions T_3 and T_4. The root-mean-square deviation of experimental and calculated line positions was ~ 0.13 Hz.

The pyrimidine spectrum, Fig. 2, exhibits 22 distinct lines. The complexity of the pattern prohibited determination of parameters directly from the spectrum. A trial set of dipolar couplings was calculated from an approximate structure and an estimated set of

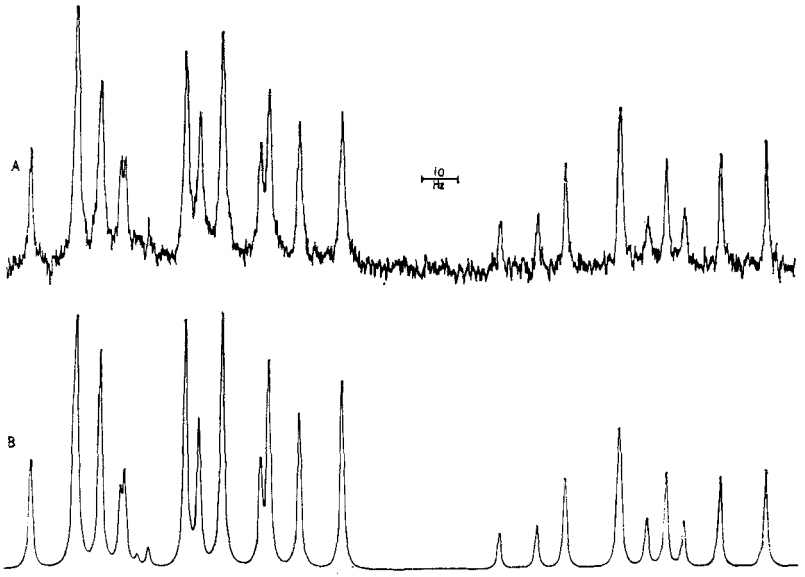


Figure 2. Experimental (A) and calculated (B) spectrum of pyrimidine partially oriented in the lyotropic mesophase.

motional constants. The motional constants were then varied until a visual simulation of the experimental spectrum was obtained. The initial values of indirect couplings and chemical shift differences were those of Reddy, Hobgood, and Goldstein.[17] Since the spectrum was insensitive to J_{13} and J_{24}, these were given values of 1.00 Hz and 2.00 Hz, respectively. The final set of parameters for each temperature was determined by a least squares fit of the experimental and calculated line frequencies. These parameters are presented in Table 2. The rms error between experimental and calculated line

TABLE 2 NMR Parameters and Motional Constants for Pyrimidine

	293 °K[a]	305 °K[a]	311 °K[b]	315 °K[a]
$\delta(w_3 - w_1)$[c]	1.64 ±0.001	1.65 ±0.001	1.65 ±0.002	1.66 ±0.001
$\delta(w_3 - w_2)$	1.25 ±0.001	1.26 ±0.001	1.26 ±0.001	1.27 ±0.001
J_{12}	0.5 ±0.1	0.4	0.4 ±0.1	0.2
J_{13}[d]	1.0	1.0	1.0	1.0
J_{23}	6.8 ±0.3	7.6	5.3 ±0.4	6.5
J_{24}[d]	2.0	2.0	2.0	2.0
D_{12}	−12.88 ±0.04	−10.23	−8.87 ±0.06	−7.93
D_{13}	−13.90 ±0.05	−11.33	−10.10 ±0.09	−9.30
D_{23}	20.88 ±0.34	20.62	23.12 ±0.49	22.89
D_{24}	13.99 ±0.04	12.78	12.26 ±0.04	12.03
$C_{3z^2-r^2}$[e]	0.01554 ±0.00008	0.01273	0.01145 ±0.0001	0.01042
$C_{x^2-y^2}$	0.00277 ±0.00006	0.00338	0.00368 ±0.00007	0.00408

[a] Spectra taken at 90 MHz

[b] Spectra taken at 60 MHz.

[c] Chemical shift differences in ppm.

[d] Cannot be determined from the spectrum; J_{ij} and D_{ij} are in Hertz.

[e] Calculated in the molecule fixed frame given in Fig. 4. r_{24} was set equal to 4.2740 Å[10] for the calculation of $C_{3z^2-r^2}$ and $C_{x^2-y^2}$.

positions for data at a given temperature was no greater than ~ 0.2 Hz. The absolute signs of the D_{ij} were determined unambiguously relative to positive J_{ij} values.[18]

The pyridazine spectrum, Fig. 3, consists of 16 well-resolved lines. The chemical shift difference between the protons α and β to the nitrogen atoms introduces considerable asymmetry into the spectrum. In this case, as for pyrimidine, an assumed geometry was substituted into the equations for the dipolar couplings and the motional

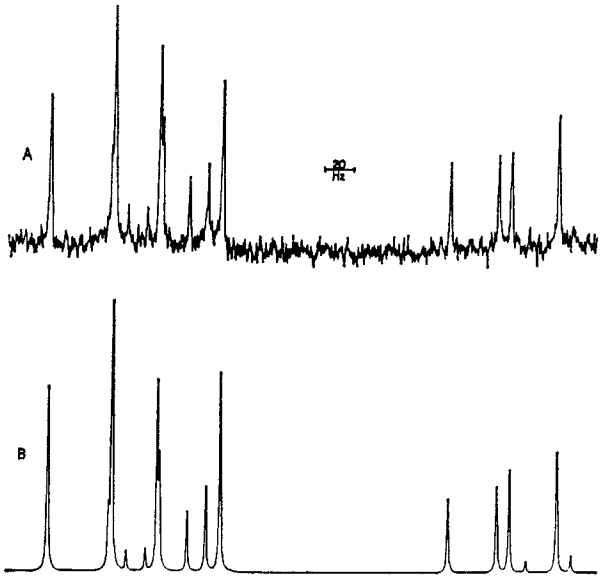


Figure 3. Experimental (A) and calculated (B) spectrum of pyridazine oriented in the lyotropic mesophase.

constants for pyrimidine taken as an initial estimate. The indirect couplings were those reported by Gil and Pinto.[19] The chemical shift difference between the α and β protons used initially was that reported by Tori *et al.*[18] The parameters were varied until an acceptable simulation of the experimental spectrum was obtained and the parameters refined by the least-squares procedure. The parameters which satisfactorily reproduce the observed spectrum are presented in Table 3. All parameters except J_{14} and J_{23} were varied during the final iterations. These values were not determined; and were set equal to 1.4 Hz and 8.3 Hz, respectively.[19]

TABLE 3 NMR Parameters and Motional Constants for Pyridazine

	294 °K[a]	305 °K[b]	309 °K[b]	314 °K[b]
$\delta(w_2 - w_1)$ [c]	1.494 ±0.002	1.500 ±0.002	1.501 ±0.002	1.501 ±0.002
J_{12}	5.1 ±0.1	5.0 ±0.2	5.2 ±0.2	6.4 ±0.6
J_{13}	1.9 ±0.1	2.0 ±0.2	1.7 ±0.2	0.5 ±1.0
J_{14} [d]	1.4	1.4	1.4	1.4
J_{23} [d]	8.3	8.3	8.3	8.3
D_{12}	−46.11 ±0.29	−35.75 ±0.30	−31.99 ±0.30	−28.35 ±0.30
D_{13}	−24.93 ±0.31	−20.50 ±0.30	−19.63 ±0.30	−17.49 ±0.30
D_{14}	−23.19 ±0.10	−19.85 ±0.10	−18.56 ±0.10	−17.30 ±0.10
D_{23}	−159.17 ±0.28	−134.35 ±0.30	−126.52 ±0.30	−116.91 ±0.30
$C_{3z^2-r^2}$ [e]	+0.00148	+0.00129	+0.00044	+0.00086
	±0.00042	±0.00042	±0.00042	±0.00040
$C_{x^2-y^2}$	−0.02368	−0.02001	−0.01840	−0.01726
	±0.00026	±0.00026	±0.00026	±0.00026

[a] Couplings are in units of Hertz.

[b] Uncertainties in D_{ij}, $C_{3z^2-r^2}$, and $C_{x^2-y^2}$ are set at the uncertainty of the 294 °K data since fewer scans were taken at 305°, 309°, and 315 °K

[c] Chemical shift difference in ppm.

[d] Values held fixed during final iterations.

[e] Calculated in the molecule fixed frame (Fig. 4). r_{23} was set equal to 2.3716 Å the microwave value [14] for the calculation of $C_{3z^2-r^2}$ and $C_{x^2-y^2}$.

4. Geometry

The anisotropic motion of pyrazine, pyrimidine, and pyridazine can be described by two motional constants, provided we choose the molecule-fixed axis systems illustrated in Fig. 4. In these coordinate systems only $C_{3z^2-r^2}$ and $C_{x^2-y^2}$ are non-zero.[20] In the present investigation vibrational motions of the nuclei and the anisotropic contributions to the indirect coupling constants have been neglected as is common practice. The shape of a molecule under consideration is related to the direct coupling constant through the expression introduced by Snyder.[20] Elimination of the motional

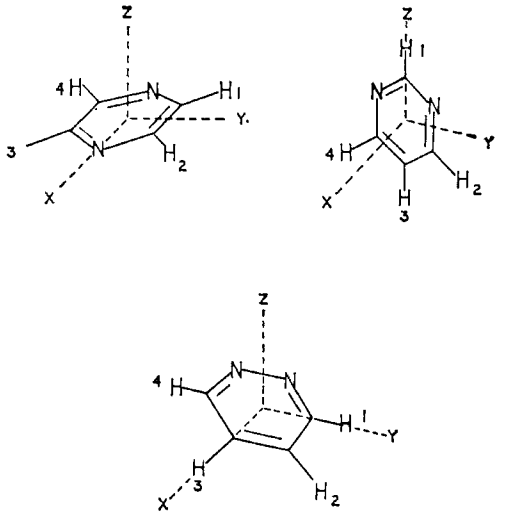


Figure 4. Coordinate system for pyrazine, pyrimidine, and pyridazine.

constants from the set of equations for each molecule reveals that, in addition to the motional constants, one interproton distance ratio can be determined for pyrazine, (r_{14}/r_{12}); three distance ratios for pyrimidine, (r_{12}/r_{23}), (r_{13}/r_{23}), (r_{24}/r_{23}); and three for pyridazine, (r_{12}/r_{23}), (r_{13}/r_{23}), and (r_{14}/r_{23}). For the calculation of motional constants one proton–proton distance in the molecule determined from a different method is required. The motional constants were calculated from the following relations:

Pyrazine

$$C_{3z^2-r^2} = 2^{-1} \cdot 5^{1/2} K_{ij}^{-1} r_{12}^3 [D_{14}(r_{14}/r_{12})^3 + D_{12}]$$
$$C_{x^2-y^2} = 3^{-1/2} [K_{ij}^{-1} \cdot 5^{1/2} D_{14} r_{12}^3 (r_{14}/r_{12})^3 - C_{3z^2-r^2}].$$

Pyrimidine

$$C_{3z^2-r^2} = -2^{-1} \cdot 5^{1/2} K_{ij}^{-1} r_{24}^3 (r_{13}/r_{24})^3 D_{13}$$
$$C_{x^2-y^2} = 3^{-1/2} [K_{ij}^{-1} \cdot 5^{1/2} D_{24} r_{24}^3 - C_{3z^2-r^2}].$$

Pyridazine

$$C_{3z^2-r^2} = 2^{-1} \cdot 5^{1/2} K_{ij}^{-1} r_{23}^3 \langle (D_{23}/4)[(D_{23}/D_{14})^{1/3} - 1]^2 - D_{12}(r_{12}/r_{23})^5 \rangle \cdot \{(r_{12}/r_{23})^2 - 1/4[(D_{23}/D_{14})^{1/3} - 1]^2\}^{-1}$$

$$C_{x^2-y^2} = 3^{1/2}(5^{1/2} D_{23} r_{23}^3 K_{ij}^{-1} - C_{3z^2-r^2}).$$

The values of r_{12} (2.4375 Å) for pyrazine, r_{24} (4.2740 Å) for pyrimidine, and r_{23} (2.3716 Å) for pyridazine in the above equations were taken from Refs. 21, 10, and 14, respectively.

Equations from which the distance ratios were determined have been published previously and are presented below for ready reference.

Pyrazine (Ref. 22)

$$D_{14}(r_{14}/r_{12})^5 - D_{13}[1 + (r_{14}/r_{12})^2]^{5/2} + D_{12} = 0.$$

Pyrimidine (Ref. 10)

$$D_{12}[1/4Y^2 + \{[(D_{23} - 1/4Y^5 D_{24})/D_{13}(1 - 1/4Y^2)]^{1/3} - (1 - 1/4Y^2)^{1/2}\}^2]^{5/2} - 1/4Y^5 D_{24} - [(D_{23} - 1/4Y^5 D_{24})/(1 - 1/4Y^2)] \cdot [\{(D_{23} - 1/4Y^5 D_{24})/D_{13}(1 - 1/4Y^2)\}^{1/3} - (1 - 1/4Y^2)^{1/2}]^2 = 0.$$

$$(r_{13}/r_{23}) = \{[D_{23} - 1/4Y^5 D_{24}]/(1 - 1/4Y^2)D_{13}\}^{1/3}$$
$$(r_{12}/r_{23}) = \{1/4Y^2 + [(r_{13}/r_{23}) - (1 - 1/4Y^2)^{1/2}]^2\}^{1/2}.$$

The quantity Y equals (r_{24}/r_{23}).

Pyridazine (Ref. 23)

$$(r_{14}/r_{23}) = (D_{23}/D_{14})^{1/3}$$
$$(r_{13}/r_{23})^2 = (D_{23}/D_{14})^{1/3} + (r_{12}/r_{23})^2$$
$$D_{12}(r_{12}/r_{23})^5 - D_{13}[(D_{23}/D_{14})^{1/3} + (r_{12}/r_{23})^2]^{5/2} + D_{23}(D_{23}/D_{14})^{1/3} = 0.$$

The distance ratios for pyrazine, pyrimidine, and pyridazine were determined numerically from the appropriate relations above and given in Table 4.

TABLE 4 Distance Ratios for Pyrazine, Pyrimidine and Pyridazine

	NMR Lyotropic	NMR Thermotropic[a]	X-ray[b]	Microwave[c]
Pyrazine				
(r_{14}/r_{12})	1.651 ±0.004	1.66 ±0.02	1.703	—
Pyrimidine				
(r_{12}/r_{23})	1.6805 ±0.013	1.62 ±0.01	1.670	1.695
(r_{13}/r_{23})	1.972 ±0.011	1.90 ±0.02	1.957	1.979
(r_{24}/r_{23})	1.704 ±0.004	1.706 ±0.004	1.720	1.712
Pyridazine				
(r_{12}/r_{23})	0.983 ±0.015	0.988 ±0.010	—	1.030
(r_{13}/r_{23})	1.692 ±0.008	1.693 ±0.007	—	1.759
(r_{14}/r_{23})	1.897 ±0.004	1.890 ±0.004	—	2.033

[a] Thermotropic values for pyrazine, pyrimidine, and pyridazine taken from Refs. 22, 10, 25, and 11 respectively.

[b] X-ray data is from Refs. 12, 13.

[c] Microwave distance ratios for pyrimidine were reported in Ref. 25. The values for pyridazine were calculated from the model proposed in Ref. 14.

5. Discussion

A. NMR Parameters and Structures

The isotropic coupling parameters for pyrazine reported by Tori and Ogata[18] are $J_{12} = 1.8$ Hz, $J_{13} = 1.8$ Hz, and $J_{14} = 0.5$ Hz. The sum, $J_{13} + J_{14}$, is + 2.30 Hz. As previously mentioned, the spectrum obtained in the liquid crystalline medium is moderately dependent on the sum, $(J_{13} + J_{14})$, and is insensitive to J_{12}. The sum determined from the liquid crystal spectrum is 1.81 Hz. The values for pyrimidine, J_{12} and J_{23}, averaged over the temperature range studied are 0.4 Hz and 6.6 Hz, respectively, compared with the isotropic solution values of ~ 0 and 5 Hz.[17] The chemical shift differences $\delta(w_3 - w_1)$ and $\delta(w_3 - w_2)$ of 1.65 and 1.25 ppm are slightly smaller than the isotropic values, 1.90 and 1.42 ppm, determined in chloroform solution. The values determined by Khetrapal, Patankar, and

Diehl for pyrimidine are 1.73 and 1.30 ppm using a thermotropic nematic solvent.[10] The effect of the anisotropic motion on the chemical shift difference is at most 0.3 ppm. The chemical shift difference, $\delta(w_2 - w_1)$, for pyridazine in the lyotropic liquid crystal case is 1.50 ± 0.002 ppm over the whole range of variation in the motional constants. The contribution to the chemical shift difference due to the anisotropic tumbling of the molecule appears to be insignificant over the temperature range employed here. The value of $\delta(w_2 - w_1)$ for the isotropic solution spectrum is 1.70 ppm,[18] whereas the value determined by Burnell and DeLange[11] in a nematic solvent at 60 °C is 1.899 ± 0.008 ppm. Considering experimental precision, the difference of about 0.4 ppm between the lyotropic and thermotropic values is significant and can be explained in terms of the increased orientation in the thermotropic nematic liquid crystal solvent. However, caution should be exercised in the interpretation of these differences due to solvent and temperature effects.[24]

The distance ratio (r_{14}/r_{12}) for pyrazine (1.651 ± 0.004) is in good agreement with the value of 1.66 ± 0.02 determined by Diehl *et al.* in the thermotropic liquid crystal at 55 °C.[23] The value calculated from X-ray data[12] is considerably larger, 1.703. It should be noted that in this case the X-ray analysis located the hydrogen positions. However, no estimates of the standard deviations of the hydrogen atom coordinates were given. Using the reported uncertainty in X-ray values for the CCH angle ($\pm 1.0°$), the C–C distance (± 0.02), and assuming the uncertainty in the C–H distance (± 0.02), an uncertainty of ± 0.09 in (r_{14}/r_{12}) can be calculated. In view of this estimated uncertainty, the NMR and X-ray data appear to agree within experimental error.

In the case of pyrimidine, the NMR values determined in the present study, the X-ray values calculated from the data of Wheatley[13] and the microwave values[25] are in excellent agreement (Table 4). The agreement between the X-ray and the NMR value is surprising, in view of the different media used and considering that the hydrogen atom coordinates were introduced into the X-ray analysis with no further refinement. The NMR values determined by Khetrapal and co-workers[10] for (r_{12}/r_{23}) and (r_{13}/r_{23}) of 1.62 ± 0.01 and 1.90 ± 0.02 are significantly different from those determined in the present investigation. The above workers were inclined to

question the reliability of the microwave values based on the small number of isotopically substituted molecules employed in the structural analysis. By contrast, the present results are in good agreement with the microwave values.

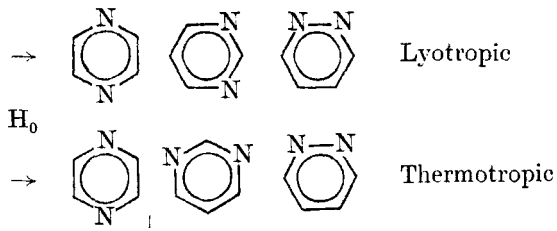
The distance ratios for pyridazine determined employing the lyotropic and thermotropic nematic phases are in excellent agreement. The microwave values, based on the model presented by Innes and Lucas,[14] are significantly different (Table 4). Although geometries deduced from microwave and NMR methods are expected to be slightly different,[22] we have observed very close agreement between values determined by both methods in the case of furan,[5] thiophene[5] and pyrimidine. The distance ratios for pyridazine determined from two NMR experiments employing different orienting media are in extremely good agreement. Under these circumstances we tend to favor the NMR values.

B. Orientation

The probability per unit solid angle that the applied field direction is at an orientation θ and ϕ in spherical polar coordinates related to the molecule fixed coordinate system is given below for pyrazine (311 °K), pyrimidine (293 °K), and pyridazine (294 °K), respectively

$$P_{311}(\theta, \phi) = 0.07895 + 0.00195 \cos^2\theta - 0.00300 \sin^2\theta \cos 2\phi$$
$$P_{293}(\theta, \phi) = 0.07822 + 0.00415 \cos^2\theta + 0.00043 \sin^2\theta \cos 2\phi$$
$$P_{294}(\theta, \phi) = 0.07973 + 0.00040 \cos^2\theta - 0.00365 \sin^2\theta \cos 2\phi.$$

These functions have maximum values when the applied magnetic field is parallel to the ring plane on the average. This is analogous to the orientation of these molecules in thermotropic nematic liquid crystals.[9-11] The most probable field direction has been sketched



above for these molecules in both lyotropic and thermotropic phases.

The most probable orientation of planar cyclic systems in thermotropic liquid crystals is such that the molecular plane is parallel to the applied field direction. In contrast, the orientation of benzene, furan, thiophene, and *p*-dithiin in this lyotropic medium is such that the most probable field direction is perpendicular to the molecular plane. If similar orienting forces were responsible for the orientation of the above mentioned molecules in the lyotropic medium, one would expect the diazines to orient in a analogous manner.

It is often assumed that the shape of the solute molecule is the dominating factor controlling orientation in thermotropic liqiud crystals. For large elongated molecules the long axis orients parallel to the optical axis of the liquid crystal. As Saupe has pointed out this rule does not always hold for small molecules.[26] Acetylene and ethylene are notable exceptions.[27,28] Studies of chloro- and fluoro-substituted benzene derivatives show that the orientation and therefore the interaction potential energy associated with orientation can be correlated with localized contributions from substituent bonds.[29,30] Results on 1,2,3-trichlorobenzene in different nematic solvents of positive and negative dielectrical anisotropy indicate that the average orientation of the principle molecular axis system is not dependent on the solvent. This evidence in conjunction with work on ortho and meta difluorobenzene shows that permanent dipole moments are of minor importance.[26]

Robertson, Yim and Gilson have extended the treatment of Saupe to include molecular shape by the application of a simple model based on dispersion force interactions.[31] Using this model the tendency for both polar and nonpolar solute molecules to align with the longest dimension parallel to the optical axis of the solvent can be explained qualitatively. Application of this treatment to molecules including thiophene, furan, pyrazine, and pyridazine leads to a prediction of similar orientation. Such a prediction is correct for thermotropic solvents, but does not explain the different orientation of the diazines in the lyotropic phase used in the present study. It appears that different orienting factors are involved for molecules which are hydrocarbon soluble and those which are water soluble. Additional studies are underway to determine the nature of these factors.

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