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

NMR Studies of Various Solutes in a Lyotropic Mesophase

Robert C. Long Jr. [a b] & J. H. Goldstein [a]

[a] Chemistry Department, Emory University Atlanta, Georgia, 30322

[b] Postdoctoral Fellow, Emory University, 1972-1973.

Version of record first published: 21 Mar 2007.

To cite this article: Robert C. Long Jr. & J. H. Goldstein (1973): NMR Studies of Various Solutes in a Lyotropic Mesophase, Molecular Crystals and Liquid Crystals, 23:1-2, 137-154

To link to this article: http://dx.doi.org/10.1080/15421407308083367

Molecular Crystals and Liquid Crystals. 1973. Vol. 23, pp. 137–154

NMR Studies of Various Solutes in a Lyotropic Mesophase†

ROBERT C. LONG, JR.‡ and J. H. GOLDSTEIN

Chemistry Department
Emory University
Atlanta, Georgia 30322

Received November 1, 1972

Abstract—High resolution nuclear magnetic resonance spectroscopy of solute molecules in ordered media has in the past been largely confined to the use of thermotropic liquid crystals as the solvent. A valuable alternate approach involving the use of a lyotropic mesophase was first reported by Lawson and Flautt, but has since been largely neglected. The present paper describes results of studies carried out for several diazines, furan, thiophene, *p*-dithiin, sodium methylphosphonate, methanol and acetonitrile. Comparisons are presented of results obtained here and in work based on the use of thermotropic media. These studies clearly demonstrate the utility of the lyotropic phase for obtaining reliable structural information. The orientations of the various solutes studied over a range of temperatures depend not only on molecular shape, but specific solute–solvent interactions.

1. Introduction

The utility of NMR methods in a wide range of applications is well known. Equally well known is the fact that such studies when carried out in ordered media greatly extend the usefulness of NMR techniques. Heretofore almost all high resolution NMR work in ordered phases has been carried out in thermotropic liquid crystals. A few years ago, however, Lawson and Flautt reported[1] the first use of a lyotropic liquid crystal phase as a solvent for high resolution NMR studies.

The phase used was derived from C_8 or C_{10} sodium alkyl sulfates, the corresponding alcohol, sodium sulfate and water. Other studies using this medium did not soon materialize, perhaps because the phase was difficult to prepare, or because it was felt that the low

† Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

‡ Postdoctoral Fellow, Emory University, 1972–1973.

degree of ordering as well as the limited solubility of the solute would restrict its utility.

During the past 2 years work in our laboratory has demonstrated that the above lyotropic phase can be advantageously employed in a variety of problems, as will become apparent in the various spectra that are to be shown here. The typical line-widths are considerably smaller than those commonly encountered in thermotropic spectra This feature arises from the fact that rapid sample spinning to achieve higher field homogeneity is possible in the lyotropic but not normally in the thermotropic media, except when superconducting magnets are used.

Previous work in this mesophase has been mainly confined to orientational studies. These include: methyl halides[2] tribromo and trichloro-benzene,[3] dimethyl sulfoxide and acetone,[4] ethanol[5] and dimethyl acetamide.[6]

Structural data have been reported for benzene[7] and thiophene[8] by other workers, and have been obtained for nine molecules by us.[9]

Because of the lack of data, comparisons of these results with those of standard structural methods is not always possible. Where it has been possible such comparisons may provide insights into the influence of environment on structure, the effect of different modes of vibrational averaging and similar questions of current interest.

In this paper, we shall survey the results of our NMR studies in the lyotropic phase and discuss, in a preliminary fashion, some of the features of the results obtained.

2. Experimental

The compounds used in this study were purchased from commercial sources and purified, where necessary, by standard procedures. The pmr spectra of all compounds employed revealed no detectable impurities. Commercial methyl phosphonic acid was neutralized with sodium hydroxide followed by recrystallization from anhydrous ethanol. The carbon-13 enriched phosphonate was prepared from 60% enriched methyl iodide as described previously.[10]

The lyotropic mesophase was prepared as reported earlier.[9a] The composition was 50% D_2O, 40% sodium decyl sulfate, 5% deuterated decanol and 5% sodium sulfate by weight. The solutes were added

to the prepared mesophase in 5 mm pmr tubes, and the solution centrifuged back and forth to achieve thorough mixing. All samples were allowed to equilibrate for several hours before initial spectra were taken.

Spectra were obtained on a Varian A-60-A nuclear magnetic resonance spectrometer operating at 60 MHz, or a Bruker HFX-90 instrument. Calibration of resonance lines was accomplished by usual techniques. Temperature control was achieved by the passage of a stream of dry N_2 over the sample. The sample temperature was monitored by a thermocouple close to the sample which had been previously calibrated by a standard ethylene glycol sample, the uncertainty being ± 0.5 °C.

Analysis of spectra was carried out with the aid of a Digital Equipment Corporation PDP-10 computer using a version of LAOCN3 modified to include dipole–dipole couplings.

3. Results and Discussion

A) Structure

In the cases of furan, thiophene, pyrazine, pyrimidine and pyridazine, each possesses two perpendicular planes of symmetry, the proper choice of a cartesian molecule-fixed axis system guarantees that only two motion constants, $C_{3z^2-r^2}$, and $C_{x^2-y^2}$, are needed to describe the anisotropic motion of the molecule.[11] With the exception of pyrazine, in the above molecules the z-axis is taken as the C_2 axis in the molecular plane with the y-axis in the molecular plane and the x-axis perpendicular to the plane.

For pyrazine, the z-axis was taken perpendicular to the molecular plane with the x-axis passing through both nitrogens. The anisotropic motion of the remainder of the compounds possessing an effective threefold axis can be described by only one motional constant, $C_{3z^2-r^2}$.[11] In this case, the z-axis is taken as the threefold axis.

The expression employed for dipolar couplings in terms of the motional constants and nuclear coordinates is that of Snyder,[11] and will not be repeated here.

The calculations were performed with neglect of vibrational corrections as well as anisotropies of indirect couplings.[12]

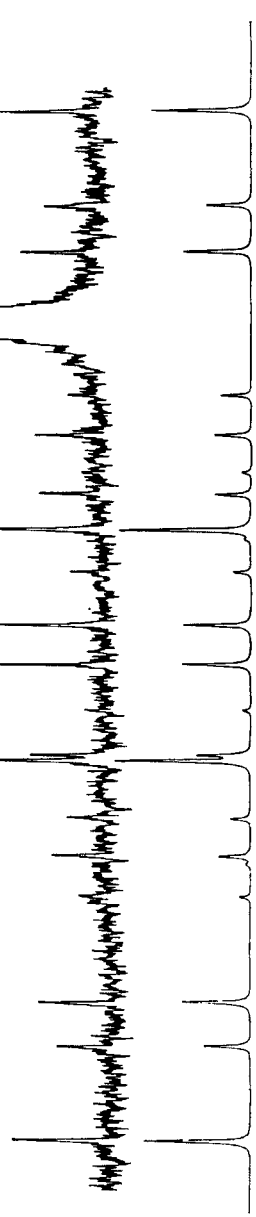


Figure 1. Experimental spectrum (upper) and calculated spectrum (lower) of thiophene in the lyotropic mesophase (1.2% by weight; 38 °C; single scan).

Shown in Fig. 1 is the experimental spectrum of a 1.2% by weight sample of thiophene obtained in a single scan. The pattern for furan is similar and will not be given. The spectrum of thiophene consists of 22 well resolved lines, usually of 1–2 Hz line-width, as compared with about 4–50 Hz line-width in the usual thermotropic experiments. The calculated spectrum for the $AA'BB'$ spin system appears in the lower portion of Fig. 1. The root-mean-square deviation between experimental and calculated frequencies for both cases was <0.3 Hz.

The spectral parameters for furan and thiophene are shown in Table 1. It is appropriate to remark at this point that, because of the lower degree of ordering in the phase used, the direct couplings are not as dominant in determining the spectrum as is often the case when thermotropic media are employed. One consequence of this is the fact that the signs of the J's relative to those of the D's can often be more reliably determined. The isotropic couplings for furan and thiophene are known to be positive from independent evidence.[13] Since the present study reveals that the dipolar and isotropic couplings are of the same sign, the former must also be

TABLE 1 NMR Parameters for Thiophene and Furan at 38 °C

	Thiophene	Furan
$\delta(\omega_2 - \omega_1)$	14.22 ± 0.18	65.47 ± 0.11
J_{12}[a]	4.90	1.75
J_{13}	1.04	0.81
J_{14}	2.84	1.48
J_{23}	3.50	3.27
D_{12}	140.30 ± 0.30	105.50 ± 0.21
D_{13}	48.32 ± 0.16	38.11 ± 0.10
D_{14}	51.00 ± 0.12	53.73 ± 0.12
D_{23}	256.93 ± 0.37	176.76 ± 0.30
$C_{3z^2-r^2}$[b]	-0.0195 ± 0.0004	-0.0187 ± 0.0004
$C_{x^2-y^2}$	$+0.0613 \pm 0.0003$	$+0.0506 \pm 0.0003$

[a] J_{ij} values for thiophene are from Ref. 13a and for furan from Ref. 13b. δ, J_{ij} and D_{ij} are in Hertz at 60 MHz.

[b] r_{23} was assumed to be 2.627 Å for thiophene and 2.756 Å for furan in order to calculate the motional constants, Ref. 16a, b.

positive. The importance of this result is obvious because of the dependence of the orientation on the sign of the D's.

The distance ratios obtained for furan and thiophene are given in Table 2. Also shown for comparison are the electron-diffraction,[14] microwave,[15] and NMR thermotropic[16] structural data, as well as the results of a recent study by Dereppe.[8]

TABLE 2 Distance Ratios

	r_{12}/r_{23}	r_{13}/r_{23}	r_{14}/r_{23}
Thiophene			
NMR Lyotropic[a]	0.985 ± 0.005	1.638 ± 0.003	1.714 ± 0.001
NMR Lyotropic[b]	1.031 ± 0.014	1.672 ± 0.017	1.733 ± 0.012
NMR Thermotropic[c]	0.995 ± 0.005	1.653 ± 0.006	1.745 ± 0.010
Microwave[d]	0.999 ± 0.007	1.648 ± 0.009	1.719 ± 0.018
E.D. (I)[e]	1.01 ± 0.09	1.66 ± 0.16	1.74 ± 0.17
E.D. (II)[e]	1.12 ± 0.17	1.77 ± 0.28	1.88 ± 0.28
Furan			
NMR Lyotropic[a]	0.985 ± 0.006	1.567 ± 0.004	1.487 ± 0.004
NMR Thermotropic[c]	0.98 ± 0.02	1.56 ± 0.02	1.47 ± 0.02
Microwave[d]	0.992 ± 0.001	1.572 ± 0.002	1.486 ± 0.001

[a] Present investigation; [b] Ref. 8; [c] Ref. 16a, b; [d] Ref. 15a, b; [e] Ref. 14.

TABLE 3 Spin-Hamiltonian Parameters for Pyrazine at 38 °C

$\delta(\omega_1 - \omega_2)$	0.00
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° (28). The molecule-fixed axis system is given in Fig. 5.

The agreement shown is quite satisfactory except for electron-diffraction results, where two different sets of structural data have been reported. In general one would expect better agreement with microwave results and poorer agreement with electron-diffraction results because of the nature of the vibrational averaging processes for structural parameters.

A typical spectrum, representative of the diazines, is shown in Fig. 2 for pyridazine. The spectral parameters for the diazines are given in Tables 3, 4, 5. The structural results for all three diazines are presented in Table 6. This series is not an ideal one for interpreting structural results since pyrazine has no microwave spectrum, and

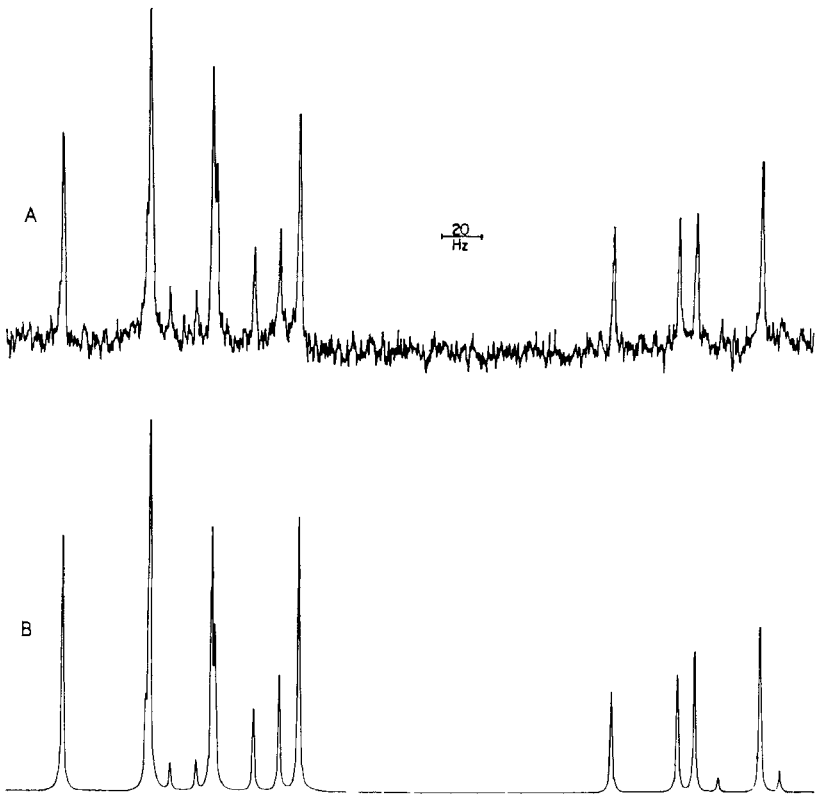


Figure 2. Experimental spectrum (upper) and calculated spectrum (lower) of pyridazine in the lyotropic mesophase (0.68% by weight; 21 °C; single scan).

TABLE 4 NMR Parameters and Motional Constants for Pyrimidine

	20 °C[a]	32 °C[a]	38 °C[b]	42 °C[a]
$\delta(\omega_3-\omega_1)$[c]	1.64 ±0.001	1.65 ±0.001	1.65 ±0.002	1.66 ±0.001
$\delta(\omega_3-\omega_2)$	1.25 ±0.001	1.26 ±0.001	1.26 ±0.002	1.27 ±0.001
J_{12}	0.51 ±0.02	0.40	0.36 ±0.10	0.20
J_{13}[d]	1.42	1.42	1.42	1.42
J_{23}	7.1 ±0.5	7.56	5.50 ±0.31	6.47
J_{24}[d]	2.5	2.5	2.5	2.5
D_{12}	−12.89 ±0.03	−10.22	−8.85 ±0.06	−7.92
D_{13}	−14.32 ±0.05	−11.75	−10.53 ±0.09	−9.73
D_{23}	20.68 ±0.49	20.65	23.24 ±0.30	22.90
D_{24}	13.99 ±0.04	12.78	12.26 ±0.04	12.03
$C_{3z^2-r^2}$[e]	0.01522 ±0.00006	0.01248	0.01120 ±0.00007	0.01025
$C_{x^2-y^2}$	0.00296 ±0.00005	0.00353	0.00382 ±0.00006	0.00418

[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. 5. r_{24} was set equal to 4.2740 Å[29] for the calculation of $C_{3z^2-r^2}$ and $C_{x^2-y^2}$.

TABLE 5 NMR Parameters and Motional Constants for Pyridazine

	21 °C[a]	32 °C[b]	36 °C[b]	41 °C[b]
$\delta(\omega_2-\omega_1)$[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
$C_{3z^2-r^2}$	+0.00148 ±0.00042	+0.00129 ±0.00042	+0.00044 ±0.00042	+0.00086 ±0.00040
$C_{x^2-y^2}$	−0.02368 ±0.00026	−0.02001 ±0.00026	−0.01840 ±0.00026	−0.01726 ±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 21 °C data since fewer scans were taken at 32°, 36°, and 41 °C.

[c] Chemical shift difference in ppm.

[d] Values held fixed during final iterations.

[e] Calculated in the molecule fixed frame Fig. 5. r_{23} was set equal to 2.3716 Å the microwave value[30] for the calculation of $C_{3z^2-r^2}$ and $C_{x^2-y^2}$.

the model on which the pyridazine microwave structure was based may be subject to some uncertainty. We have also found that the lyotropic values are independent of temperature over the range studied. The similarity shown here between lyotropic and thermotropic ratios for pyridazine is the best agreement obtained for the series of molecules studied.

TABLE 6 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})	1.642 ±0.011	1.62 ±0.01	1.670	1.695
(r_{13}/r_{23})	1.930 ±0.009	1.90 ±0.02	1.957	1.979
(r_{24}/r_{23})	1.701 ±0.005	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. 12, 29 and 33 respectively.

[b] X-ray data is from Ref. 34a, b.

[c] Microwave distance ratios for pyrimidine were reported in Ref. 32. The values for pyridazine were calculated from the model proposed in Ref. 30.

The final molecules for which structural results are described here is the methyl phosphonate anion. Figure 3 shows the composite pattern of the proton spectrum plus the ^{13}C—H satellite spectrum of a 60% ^{13}C enriched molecule. The ^{13}C spectrum of the same molecule is presented in Fig. 4. This spectrum represents 256 accumulations on the solution in a 10 mm tube. However, the couplings were measured from spectra covering 2 Hz/cm.

The spectra were taken at a pH corresponding to about 26% protonation of the dianion; the pH of the phase was 7.46 at 25 °C. Under these conditions the patterns are consistent with effective C_{3v} symmetry. The spectra are easily interpreted using the first order splitting diagram shown at the top of the figures.

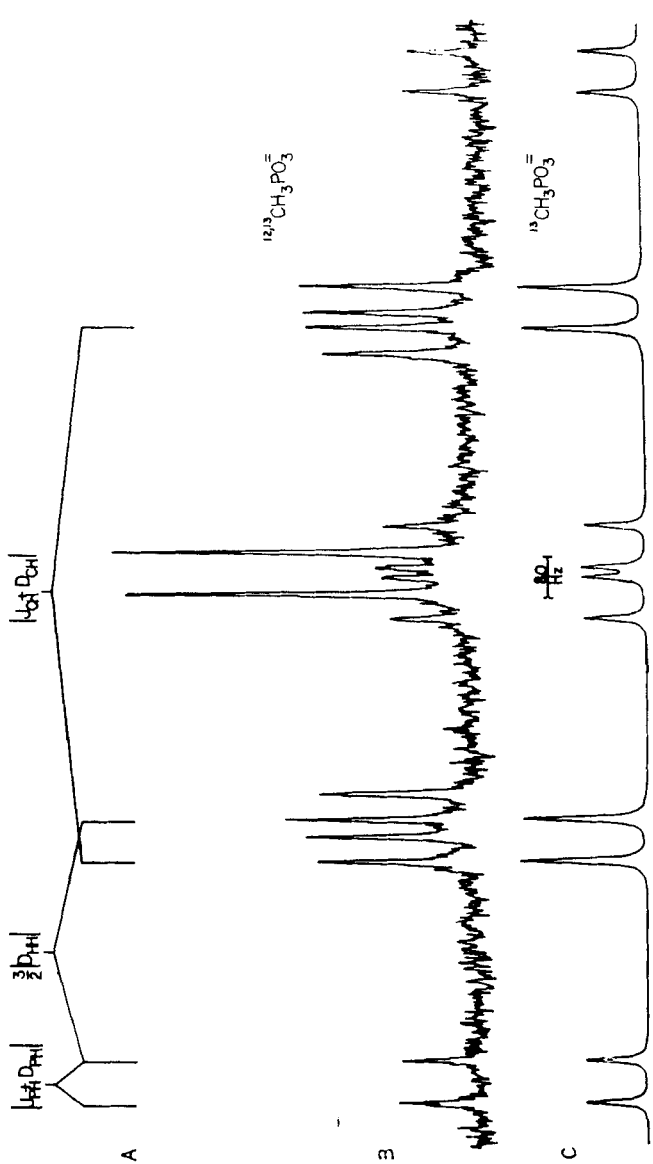


Figure 3. ^{13}C—H satellite spectrum of 60% enriched sodium methyl phosphonate in the lyotropic phase (1.84% by weight; 46 °C; single scan). Experimental spectrum (upper) and the calculated spectrum for the ^{13}C species (lower).

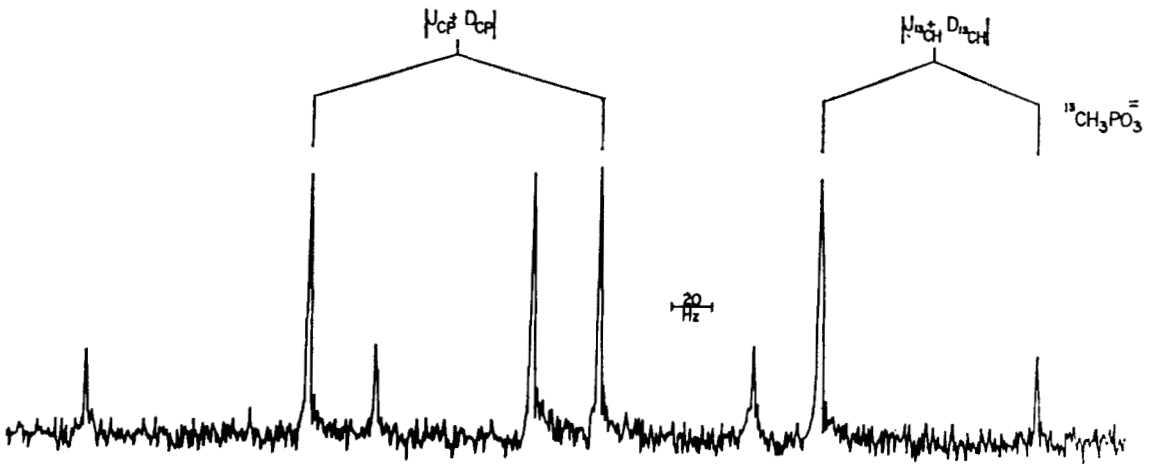


Figure 4. ^{13}C spectrum of 60% enriched sodium methyl phosphonate (1.84% by weight; 21 °C; 10 mm tube; 256 scans).

The results obtained are given in Table 7. The relative signs of all the couplings are in fact absolute since that of J_{CH} is known to be positive. The present set of signs agree with those determined by McFarlane using double resonance methods.[17]

TABLE 7 Structural Parameters for Sodium Methyl Phosphonate

$|D_{PH}+J_{PH}| < |J_{PH}|$
$|D_{CH}+J_{CH}| < |J_{CH}|$

Relative signs of couplings $^{+}J_{CH}, {}^{-}D_{CH}, {}^{-}J_{PH}, {}^{+}D_{PH}, {}^{-}D_{HH}, {}^{+}J_{CP}, {}^{+}D_{CP}$	
$(r_{HH}/r_{CH}) = +1.620 \pm 0.003$	
$(r_{HH}/r_{PH}) = 0.7557 \pm 0.004$	
$(D_{CH}/D_{CP}) = -3.629 \pm 0.135$	
$\angle HCH = 108.23 \pm 0.30$[a]	
$r_{CP} = (1.576 \pm 0.009)\, r_{CH}$	(^{1}H spect)[a]
$r_{CP} = (1.68 \pm 0.03)\, r_{CH}$	(^{13}C spect)[a]
$C_{3z^2-r^2} = (-)$[b]	

[a] $\angle HCH$ and r_{CP} represent the average of data taken at 10 separate temperatures from 20°–70 °C.

[b] Details of this study will be published elsewhere.

In view of the relations for the splittings in Figs. 3, 4 the J's must be known very precisely if reliable structural data is to be obtained. The isotropic solution value of J_{PH} was -15.85 ± 0.05 over the concentration range from 1%–13% by weight in D_2O and a temperature range 38°–100 °C. The corresponding values of J_{CH} of 124.4 ± 0.2 and J_{cp} of 131.78 ± 0.2 were also insensitive to solvent and temperature effects.

It can be shown that for a temperature independent scalar coupling and geometry, the ratio of D_{HX}/D_{HH} should be constant with temperature. For a low degree of ordering use can be made of this fact in order to calculate J_{CH} and J_{PH} from the liquid crystal data, since departure from the correct J value causes a regular variation in the above ratio with temperature. The J values determined were $J_{PH} = -15.93 \pm 0.14$ and $J_{CH} = 124.6 \pm 0.6$ in good agreement with the values mentioned previously, as determined in D_2O solution.

Two quite dissimilar values of the C—P distance were obtained depending upon whether the H—H, C—H and PH coupling values used were from the ^{13}C—H satellite patterns or the CH and CP

couplings provided by the ^{13}C spectrum. If we adopt 1.09 Å as the C—H distance we can calculate from the ratios a value of 1.72 ± 0.01 and 1.83 ± 0.03, respectively.

The latter is in good agreement with the value of 1.84 ± 0.04 Å for CP single bonds.[18] The former approaches that for CP double bonds.[18] This appears to be unreasonable, but cannot be accounted for by experimental uncertainty. An analogous problem in methyl fluoride is well known and has been thought to arise from anisotropies in electron coupled indirect interactions or from the failure to correct for vibrational motion.[19–22]

B) Orientations

The orientations of the molecules studied are of considerable interest in terms of the interactions responsible for their orientation. Saupe has shown that, in thermotropic solvents, except in cases of specific interactions such as hydrogen bonding, dispersion forces are primarily responsible for alignment.[23] This implies a dependence of the orientational potential energy on polarizability anisotropies and thus on molecular shape. For large molecules the long-axis usually has the largest positive S value (S being defined as the appropriate element of the order matrix). Robertson, Yim and Gilson have calculated the effective dimensions of pyrazine, pyridazine, furan and thiophene.[24] In each case the longest dimension corresponds to the axis having the most positive S value, see Fig. 5, whereas the shortest dimension has the most negative S value.

Pyrimidine is an exceptional case since for it the largest positive S value does not correspond to the maximum molecular dimension.

However, in all the above cases in thermotropic media, the molecular plane is unambiguously oriented parallel to the optical axis.

This generalization does not hold for the same molecules in the lyotropic phase. The striking exception is that of pyridazine in which the x-axis has the most positive S value. The molecular plane is thus perpendicular to the optical axis of the mesophase. In the case of furan, thiophene, p-dithiin and tetra fluroro-1,3-dithietane in the lyotropic phase the y-axis is preferentially directed along the optical axis.

In general for the more hydrophobic molecules, the strongest

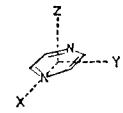
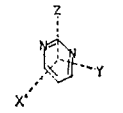
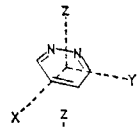
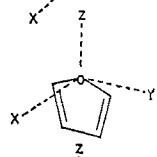
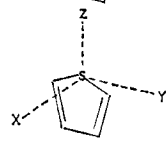
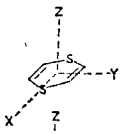
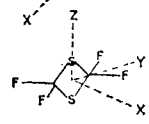
	THERMOTROPIC	LYOTROPIC	
S_{zz}	-0.0970	-0.00653	
S_{xx}	0.0408	0.01835	
S_{yy}	0.0562	-0.01182	
S_{zz}	0.0283	-0.01361	
S_{xx}	-0.0918	0.00451	
S_{yy}	0.0635	0.00910	
S_{zz}	0.0347	-0.00132	
S_{xx}	-0.0991	0.01901	
S_{yy}	0.0644	-0.01768	
S_{zz}	0.0469	0.01673	
S_{xx}	-0.0620	-0.04756	
S_{yy}	0.0151	0.03083	
S_{zz}	0.0639	0.01744	
S_{xx}	-0.0904	-0.05620	
S_{yy}	0.0265	0.03876	
S_{zz}		-0.07940	
S_{xx}		0.02534	
S_{yy}		0.05406	
S_{zz}		0.01323	
S_{xx}		-0.04632	
S_{yy}		0.03310	

Figure 5. Comparison of order parameters for solutes in thermotropic and in the lyotropic mesophase. The solutes are from top to bottom: pyrazine, pyrimidine, pyridazine, furan, thiophene, *p*-dithiin and tetrafluoro-1,3-dithietane.

tendency is for the ring containing the heteratoms to be parallel to the optical axis. This is indicated by the fact that the negative S element has the largest absolute magnitude. This is in line with the results obtained by Black, Lawson and Flautt for benzene in which the degree of order associated with the six-fold axis is -0.0803.[7] This is not the case for the more hydrophilic diazines. One of the

major points which should be made is that the orientation does not depend solely upon their shapes. It is likely that to some extent specific interactions with elements of the medium are involved. Such interactions become increasingly dominant in oriented polypeptide solutions.[25,26]

The temperature dependence of $P^{max}(\theta, \phi)$ for 1% by weight samples of a number of solutes in the lyotropic phase is given in Fig. 6. P^{max} is the maximum value of Snyder's function describing

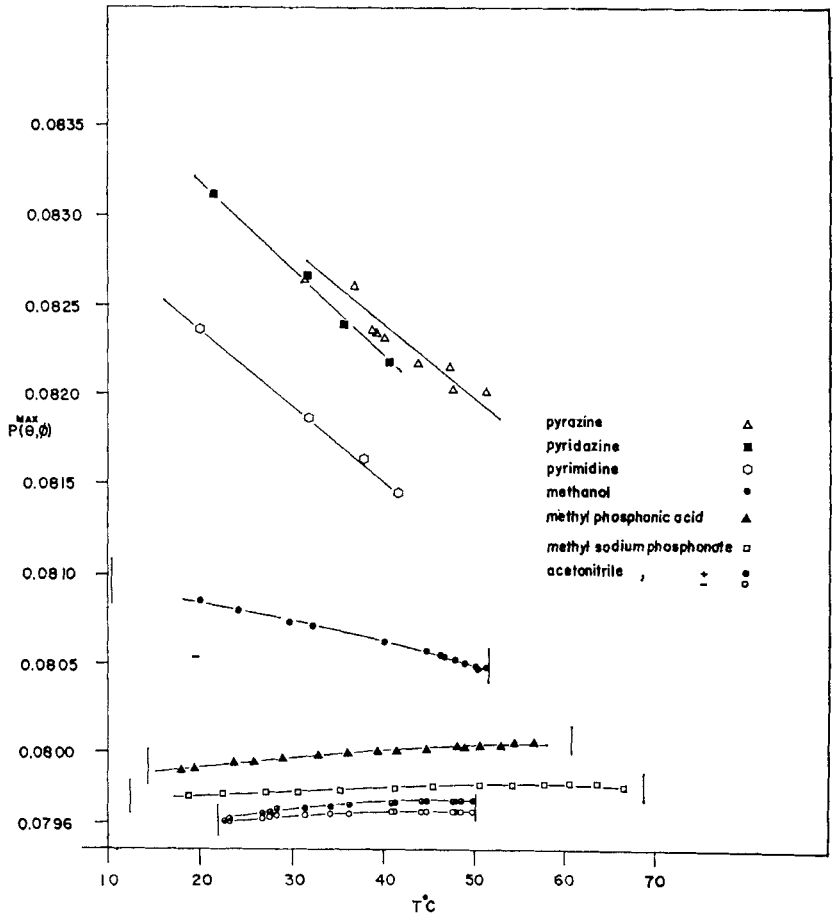


Figure 6. Temperature dependence of the order for ~1% by weight concentrations in the lyotropic phase. Vertical solid lines represent temperatures at which the order of the solute decreased to zero.

the probability of finding a molecule at a given orientation with respect to the applied magnetic field, and is a convenient measure of the order. It has the added advantage of being independent of the molecule-fixed axis system.

The temperature dependence of P^{max} increases with P^{max} itself. The more highly ordered solutes at the top are the more lipophilic molecules. Although complete temperature studies for furan, thiophene and benzene have not been completed, P^{max} increases steadily with lipophilicity. The lipid region of the mesophase is the more ordered region of the mesophase and the order is known to decrease with temperature as confirmed by line-width measurements on the lipid alkyl resonances in the same phase as a function of temperature.[27] The more hydrophilic solutes on the other hand are expected to experience a relatively low degree of order over the entire temperature range. Lindon and Dailey have reported small dipolar couplings for acetone and dimethyl sulfoxide as solutes in the same phase.[4]

Methanol and methyl phosphonic acid exhibit behavior intermediate between that of the other two groups. These are hydrophilic molecules which can act as proton donors as well as proton acceptors.

The motional constant for methanol is negative (determined from ^{13}C—H satellites of enriched methanol assuming a positive J_{CH}). Thus methanol and sodium methyl phosphonate have similar orientations with the C—O or C—P bond preferentially perpendicular to the applied magnetic field direction. If acetonitrile orients in an analogous manner with the C—C≡N unit perpendicular to the field, the motional constant would also be negative (P^{max} for both signs are given in Fig. 6).

The temperature dependence of P^{max} for methanol, methyl phosphonic acid, sodium methyl phosphonate and acetonitrile show considerable differences. The function decreases with temperature for methanol while an increase is noted for the remaining solutes.

Acknowledgements

The authors gratefully acknowledge support by a grant from the National Institutes of Health. We are most indebted to Kathryn R.

Long and Steven L. Baughcum for assistance in various phases of this work.

REFERENCES

1. Lawson, K. D. and Flautt, T. J., *J. Amer. Chem. Soc.* **89,** 5489 (1967).
2. Hayamizu, K. and Yamamoto, O., *J. Mag. Res.* **5,** 94 (1971).
3. Hayamizu, K. and Yamamoto, O., *J. Mag. Res.* **2,** 377 (1970).
4. Lindon, J. and Dailey, B. P., *Mol. Phys.* **20,** 937 (1971).
5. Black, P. J., Lawson, K. D. and Flautt, T. J., *Mol. Cryst. and Liq. Cryst.* **7,** 201 (1969).
6. Anderson, J. M. and Lee, A. C.-F., *J. Mag. Res.* **4,** 160 (1971).
7. Black, P. J., Lawson, K. D. and Flautt, T. J., *J. Chem. Phys.* **50,** 542 (1969).
8. Dereppe, J.-M., Morisse, J.-P. and Meerssche, M. V., *Org. Mag. Res.* **3,** 583 (1971).
9. (a) Long, R. C., Jr. and Goldstein, J. H., *J. Chem. Phys.* **54,** 1563 (1971); (b) Long, R. C., Jr. and Goldstein, J. H., *J. Mol. Spectros.* **40,** 632 (1971); (c) Long, R. C., Jr., Baughcum, S. L. and Goldstein, J. H., *J. Mag. Res.* **1,** 253 (1972); (d) Unpublished results.
10. Holy, A., *Coll. Czech. Chem. Comm.* **32,** 3713 (1967).
11. Snyder, L. C., *J. Chem. Phys.* **43,** 4041 (1965).
12. Diehl, P. and Khetrapal, C. L., in *NMR Basic Principles and Progress,* Vol. I, Diehl, P., Fluck, E. and Kosefeld, R., Eds., Springer-Verlag, Berlin, 1969.
13. (a) Read, J. M., Jr., Mathis, C. T. and Goldstein, J. H., *Spectrochim. Acta* **21,** 85 (1965); (b) Lunazzi, L., *Mol. Phys.* **18,** 413 (1970).
14. Harshbarger, W. and Bauer, S. H., *Acta Cryst.* **26B,** 1010 (1970).
15. (a) Bak, B. *et al.*, *J. Mol. Spectrosc.* **7,** 58 (1961); (b) Bak, B. *et al.*, *J. Mol. Spectrosc.* **9,** 124 (1962).
16. (a) Diehl, P., Khetrapal, C. L. and Lienhard, U., *Can. J. Chem.* **46,** 2645 (1968); (b) Diehl, P., Khetrapal, C. L. and Kellerhals, H. P., *Helv. Chim. Acta* **51,** 529 (1968).
17. McFarlane, W., *Proc. Roy. Soc.* **A306,** 185 (1968).
18. Corbridge, D. E., Pearson, M. S. and Walling, C., *Topics in Phosphorus Chemistry,* Interscience, New York, N.Y., 1966.
19. Krugh, T. R. and Bernstein, P. A., *J. Chem. Phys.* **52,** 4942 (1970).
20. Bulthuis, J. and MacLean, C., *J. Mag. Res.* **4,** 148 (1971).
21. Lucas, N. J. D., *Mol. Phys.* **22,** 147 (1971).
22. Ditchfield, R. and Snyder, L. C., *J. Chem. Phys.* **56,** 5823 (1972).
23. (a) Saupe, A., *Mol. Cryst.* **1,** 527 (1966); (b) Nehring, J. and Saupe, A., *Mol. Cryst. and Liq. Cryst.* **8,** 403 (1969).
24. Robertson, J. C., Yim, C. T. and Gilson, D. F. R., *Can. J. Chem.* **49,** 2345 (1971).
25. Samulski, E. T. and Tobolsky, A. V., *Liquid Crystals and Ordered Fluids,* Johnson, J. F. and Porter, R. S., Eds., Plenum Press, New York, 1970.
26. Samulski, E. T. and Berendsen, H. J. C., *J. Chem. Phys.* **56,** 3920 (1972).
27. McLachlan, L. A., Natusch, D. F. S. and Newman, R. H., *J. Mag. Res.* **4,** 358 (1971).

28. Sutton, L. E., Ed., *Chem. Soc.* (*London*), *Spec. Publ. Supl.* **18** (1965).
29. Khetrapal, C. L., Patankar, A. V. and Diehl, P., *Org. Mag. Res.* **2**, 405 (1970).
30. Innes, K. K. and Lucas, R. M., *J. Mol. Spectrosc.* **24**, 247 (1967).
31. Gil, V. M. S. and Pinto, A. J. L., *Mol. Phys.* **16**, 623 (1969).
32. Schneider, R. F., *Dissertation Abstr.* **20**, 3536 (1960).
33. Burnell, E. E. and DeLange, C. W., *Mol. Phys.* **16**, 95 (1969).
34. (a) Wheatley, P. J., *Acta Cryst.* **10**, 182 (1957); (b) Wheatley, P. J., *Acta Cryst.* **13**, 80 (1960).