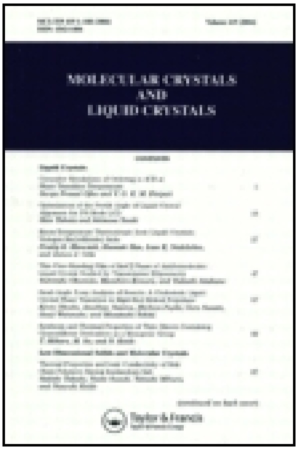

Molecular Crystals and Liquid Crystals

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

A Proton NMR Study of the Methyl Phosphonate Ion in an Amphiphilic Nematic Liquid Crystal, when the Sign of the Diamagnetic Anisotropy Changes

Keith Radley [a] [b]

[a] Department of chemistry, Simon Fraser University, Burnaby, B.C., Canada, V5A 1S6

[b] 12 New St, Skelmanthorpe, Huddersfield, W. Yorkshire, England, HD8 9BL

Version of record first published: 20 Apr 2011.

To cite this article: Keith Radley (1986): A Proton NMR Study of the Methyl Phosphonate Ion in an Amphiphilic Nematic Liquid Crystal, when the Sign of the Diamagnetic Anisotropy Changes, Molecular Crystals and Liquid Crystals, 132:3-4, 245-254

To link to this article: http://dx.doi.org/10.1080/00268948608079545

Mol. Cryst. Liq. Cryst., 1986, Vol. 132, pp. 245–254
0026-8941/86/1324-0245/$15.00/0

Printed in the United States of America

A Proton NMR Study of the Methyl Phosphonate Ion in an Amphiphilic Nematic Liquid Crystal, when the Sign of the Diamagnetic Anisotropy Changes

KEITH RADLEY†

*Department of Chemistry, Simon Fraser University, Burnaby, B.C.,
Canada V5A 1S6*

(*Received June 7, 1985*)

An abrupt change in the proton nmr dipolar couplings in methylphosphate and phenylsulphonate ions is induced in an amphiphilic nematic liquid crystal by the inclusion of the phenylsulphonate ion as the counterion. It is concluded these sign changes are due to a corresponding change in the sign of the diamagnetic anisotropy induced by the aromatic character of the phenylsulphonate ion, and not necessarily ion binding.

Keywords: methyl phosphate, NMR, amphiphilic, nematic, diamagnetism

INTRODUCTION

It is well known that the high resolution nmr of small molecules dissolved in liquid crystals enable us to determine the relative signs of the direct (*D*) and indirect (*J*) coupling constants and hence the absolute sign of *J* if the orientation of the molecules in respect to the magnetic field is reasonably well known.[1] When similar determinations are made with small molecules and ions dissolved in amphiphilic nematic liquid crystals, several factors influence the molecular orientation. Micelle structure combined with the sign of the diamagne-

---

†Present address 12 New St, Skelmanthorpe, Huddersfield, W. Yorkshire, England, HD8 9BL.

tism and to a lesser extent, the ion binding, influence the sign of the dipolar coupling constant of small molecules or ions embedded in the electrical double layer of a micelle surface.

The high resolution proton NMR spectrum of the methyl phosphonate ion will consist of a doubletted triplet. The 1:2:1 triplet line time separations will be equal to $3D_{HH}$. The dipolar coupling of the intra methyl hydrogen is

$$D_{HH} = \frac{h\gamma_H^2}{8\pi r_{HH}^3} S_{C_3}$$

where S_{C_3} is the degree of orientation of the PC axis with respect to the magnetic field and r_{HH} the distance between the methyl protons.

Each triplet peak is doubletted with a frequency separation of A, where

$$A = J_{PH} + 2D_{HH}$$

The direct coupling is

$$D_{PH} = \frac{-h\gamma_P\gamma_H}{8\pi r_{PH}^3} (3\cos^2\beta - 1)S_{C_3}$$

where r_{PH} is the distance between the phosphorus and methyl protons and β the angle between PH axis and the molecular symmetry axis.[2]

$$\frac{D_{PH}}{D_{HH}} = -3^{3/2} \sin^3\beta(2 - 3 \sin^2\beta) \frac{\gamma_P}{\gamma_H}$$

The right hand is negative since β is approximately 25° and $\gamma_P/\gamma_H > 0$, hence D_{PH} and D_{HH} have different signs. When $\beta \simeq 35°$, D_{PH}/D_{HH} has a maximum value of -0.42. When $\beta \simeq 70°$, i.e., the tetrahedral angle D_{PH}/D_{HH} changes sign. The sign and value of J_{PH} are known to be -15.85 from a previous study.[3] If the ratio D_{PH}/D_{HH} is measured in a series of samples, using the known J_{PH}, the absolute sign of the S_{C_3} is unambiguously determined.

The proton nmr spectrum of an aromatic ion such as the phenyl sulphonate ion is not simple, but it is easily analyzed using a suitable computer program where S_{xx} and S_{zz} are easily calculated from the dipolar coupling constants. The spectra are usually well enough defined to enable us to determine the absolute signs of S_{xx} and S_{zz} if the absolute signs of the J coupling are known.

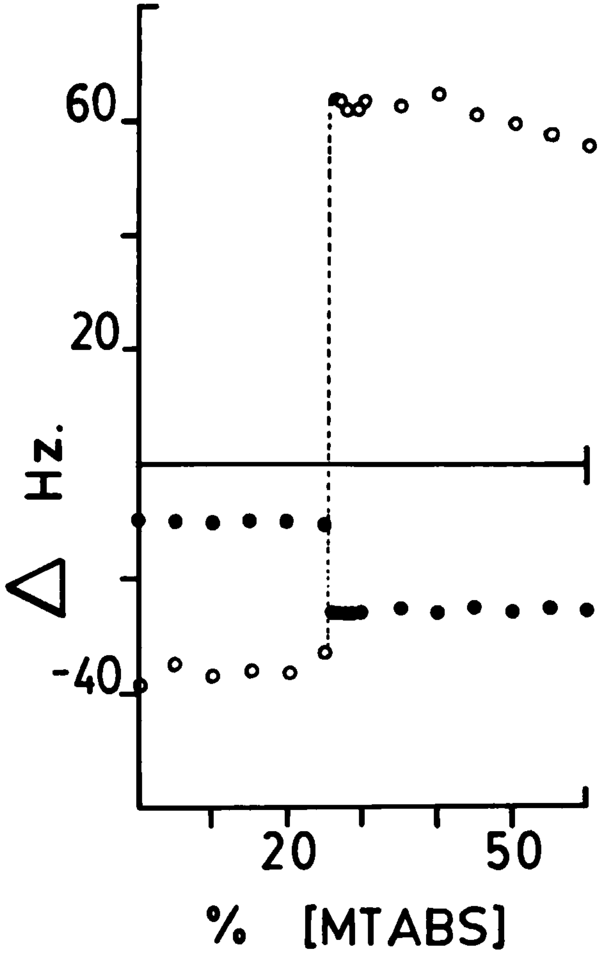

FIGURE 1 $3D_{HH}$ (○) and $2D_{HH} + J_{PH}$ (●) (Δ) from the proton nmr for the methylphosphonate ion measured in an amphiphilic nematic liquid crystal where tetradecyltrimethylammoniumphenylsulphonate (MTABS) is substituted for tetradecyltrimethylammonium bromide (MTABr), as a function of the molar % of MTABS to the total detergent.

The sign of the diamagnetic anisotropy in an amphiphilic nematic liquid crystal is changed from negative to positive by the inclusion of fluro-carbon surfactants or aromatic couterions.[4-6] When the sign of the diamagnetism changes in this way, the degree of orientation of small molecules or ions imbedded in the surface of the micelles is changed by a factor of −1/2. When the thermodynamic transition from disk to cylindrical shaped micelles takes place, the degree of orientation is predicted to change by a factor of −2. At the same time, a change in the sign of the diamagnetic anisotropy is observed so the factor of -2 is cancelled out with the $-1/2$, making no apparent change in sign or magnitude. In a *vice versa* situation, the sign still does not change but the magnitude changes by a factor of 4. Several reports have been made concerning the proton nmr spectra of solutes dissolved in thermotropic nematic mixtures where the sign of the diamagnetism is flipped by adjusting the mixture composition.[11,12]

Ion binding has been studied using samples of amphiphilic nematic liquid crystals made from mixed surfactants by changing the proportions of anionic and cationic detergents.[7,10] When the micelle surface charge is varied by changing the proportions of anionic to cationic detergents, ion binding sites are successively eliminated. A three site model has been used to analyze the quadrupolar splittings data in mixed surfactant systems.[7] It is suggested a similar multisite model could be used to analyse the dipolar coupling in terms of the ion binding of the methylphosphonate ion. In such a case, if there is a mono and multi-coordination site, the C_3 axis of methylphosphonate ion will always be parallel to the surface normal. When the binding sites are successively eliminated, no change in the sign of the dipolar coupling will be observed as $\beta \simeq 25°$. The D_{PH}/D_{HH} has a maximum value of -0.42 as already mentioned. When measured values of D_{PH}/D_{HH} are greater than -0.42, then multisite ion binding may be involved.

EXPERIMENTAL

The detergents were prepared as previously described.[8-10]. Sample compositions are provided in Tables I, II and III. The components were weighed out into test tubes and heat sealed. Double distilled D_2O was used throughout. The samples were homogeneously mixed by repeated heating and centrifuging. Samples were placed in 5 mm nmr sample tubes and the tubes heat sealed.

Nmr spectra were obtained at 25°C using a 400 MHz and 100 MHz nmr spectrometer. The 400 MHz spectrometer was used mainly for slow orienting samples. The supertron spectrometer also facilitated spinning for samples with positive diamagnetic anisotropy.

Various samples were investigated by polar microscopy at 22°C. The samples were contained in unsealed CAM LAB microslides or between a microslide and a coverslip. D_2O was allowed to evaporate from the sample edges to produce concentration gradients. This facilitates the identification of adjacent dimensionally ordered mesophases in the phase diagram. From this the structure of the micelle in the amphiphilic nematic could be inferred.

TABLE I

Mesophase composition and measured parameters of the trimethylphosphonate ion for the substitution of phenylsulphonate ions for bromide ions

Composition (Mg)[a]				NMR Parameters.(Hz)			
MOL[b]	MTABr[b]	MTABS[b]	DECANOL	$3D_{HH}$	$2D_{PH}$ + J_{PH}	$\Delta\nu_D$[c]	D_{PH}/D_{HH}
0	336	0	65	−39.0	− 9.5	2.9	−0.24
5	320	21	60	−35.5	−10.0	− 0.5	−0.25
10	303	42	60	−37.5	−10.0	− 5.9	−0.23
15	236	63	60	−36.0	−10.0	− 9.3	−0.24
20	270	83	60	−36.5	−10.0	−16.5	−0.24
25	253	104	55	−30.0	−10.8	10.7	−0.25
26	250	109	55	63.0	−25.0		−0.22
27	246	113	55	63.5	−26.0		−0.24
28	243	117	55	62.0	−26.0		−0.25
29	239	121	55	62.5	−25.5		−0.23
30	236	125	55	63.5	−25.5	30.1	−0.23
35	219	146	55	62.5	−25.0	41.8	−0.22
40	202	166	55	65.0	−26.0	45.7	−0.23
45	185	187	55	61.5	−25.0	52.0	−0.22
50	168	207	55	60.0	−25.5	56.6	−0.24
55	151	228	55	58.0	−25.0	63.1	−0.24
60	134	248	55	55.5	−25.5	67.6	−0.26

[a] Each sample was prepared with 550 mg of D_2O containing Cs_2CO_3, 2%; $CH_3PO(OH)_2$, 0.4% by weight.

[b] Tetradecyltrimethylammonium bromide, MTABr; Tetradecyltrimethylammonium, phenylsulphate; mole fraction MTABr in total detergent.

[c] ^2D nmr quadrupolar splitting of D_2O, sign assigned arbitrarily to assure smooth curve.

RESULTS AND DISCUSSION

The proton nmr spectra of the methyl phosphonate ion and the phenyl sulphonate counterion dissolved in samples of the amphiphilic nematic liquid crystals, when the bromide counterion was replaced on a molar basis by the aromatic phenyl sulphonate ion, showed an abrupt change at 25–26% molar substitution. The D_{HH} dipolar coupling doubled and the D_{PH} $(A\text{-}J_{PH})$ showed a similar change at 25–26% molar substitution (see Figure 1 and Table I). The ratio D_{PH}/D_{HH} remained constant within experimental error (-0.24 ± 0.02) across the transition. The abrupt change in the dipolar couplings was accompanied by a change in the sign of the diamagnetic anisotropy from negative to positive. The sign of the diamagnetic anisotropy was determined by observing the evolution with time of the D_2O ^2D nmr doublet from the original powder pattern. For positive diamagnetic anisotropy, the doublet evolved from the wings whereas for negative

TABLE II

Mesophase composition and measured parameters of the methylphosphonate ion in the mixed detergent system of potassium laurate/dodecyltrimethylammonium bromide

Composition (Mg)[a]					NMR Parameters. (H_2)			
MOL[b]	DoTABr[b]	DTABr[b]	KDD[b]	DECANOL	$3D_{HH}$	$2D_{PH} + J_{PH}$	$\Delta\nu_D$[c]	D_{PH}/D_{HH}
0	308		0	80	−26.1	−11.6	6.9	−0.24
10	277		24	65	−20.6	12.4	−8.1	−0.25
20	246		47	50	−14.9	13.4	−15.0	−0.25
30	216		71	30	−14.5	13.6	−22.8	−0.23
40	185		95	5	−11.9	13.7	1.2	−0.27
50		140	119	10	−14.1	−13.3	24.5	−0.27
60		112	143	0	−11.2	−13.7	68.6	−0.29
70		84	166	2	−7.0	14.4	98.5	−0.31
80	62		190	15	−7.0	14.3	141.0	−0.33
90	31		214	40	−3.9	14.9	171.0	−0.37

[a] Each sample was prepared with 900 mg of D_2O containing Cs_2CO_3, 2%; $CH_3PO(OH)_2$, 0.4% by weight.

[a] Dodecyltrimethylammoniumbromide, DoTABr; decyltrimethylammoniumbromide, DTABr; potassium dodecanoate, KDD; mol fraction KDD in total detergent, MOL:

[c] ^2D nmr quadrupolar splitting of D_2O, sign assigned arbitrarily to assure smooth curve.

TABLE III

Mesophase composition and measured parameters of the methylphosponate ion in the mixed detergent system of potassium N-dodecanoyl-*dℓ*-alaninate/tetradecyltrimethylammonium bromide

MOL[b]	KDDA[b]	TDTMABr[b]	DECANOL	$3D_{HH}$	$2D_{PH} + J_{PH}$	$\Delta\nu_D$[c]	D_{PH}/D_{HH}
0	0	336	55	−28.9	−11.1	0	−0.25
10	31	307	45	−17.7	−12.9	8.1	−0.25
20	67	270	35	−16.8	−13.0	11.6	−0.25
30	93	236	25	−14.4	−13.4	21.0	−0.26
40	124	202	15	−11.9	−13.7	32.7	−0.27
50	155	168	10	−11.8	−13.6	53.0	−0.29
60	185	134	10	−8.9	−14.5	67.5	−0.23
70	216	101	20	−7.1	−14.6	88.8	−0.26
80	247	67	40	−5.6	−14.7	114.3	−0.31
90	278	34	70	−5.4	−14.9	181.0	−0.26
100	309	0	85	−3.1	−15.5	130.4	−0.16

[a] Each sample was prepared with 850 mg of D_2O containing Cs_2CO_3, 2%; $CH_3PO(OH)_2$, 0.4% by weight.

[b] Potassium N-dodecanoyl-*dℓ*-alaninate, KDDA; tetradecyltrimethylammonium bromide, TDTMABr; MOL fraction KDDA in total detergent, MOL:

[c] ^2D nmr quadrupolar splitting of D_2O, sign assigned arbitrarily to assure smooth curve.

TABLE IV

Computer calculated parameters for the phenylsulphonate ion.

	10%[c]	55%[c]
a)		
W(1) = W(5)	−63.7	+18.8
W(2) = W(4)	−35.2	−21.9
W(3)	+0.4	+0.9
b)		
D(1,2) = D(4,5)	+1345.7	−2270.7
D(1,2) = D(3,5)	+188.6	−312.0
D(1,4) = D(2,5)	+23.9	−39.2
D(1,5) = D(2,4)	−38.4	+67.3
D(2,3) = D(3,4)	+180.3	−303.4
c)		
S_{xx}	+0.0127	−0.0223
S_{zz}	−0.0856	+0.145
S_{yy}	0.0629	−0.1227
d)		
J(1,2) = J(2,3) = J(3,4) = J(4,5)	+8.0	
J(1,3) = J(3,5)	+1.0	
J(1,4) = J(2,5)	+0.4	
J(1,5) = J(2,4)	+2.5	

[a] Chemical Shift W. (Hz)
[b] Dipolar Coupling Constants D. (Hz)
[c] Degree of Orientation S. (Hz)
[d] Indirect Coupling Constant J Assumed. (Hz)
[c] Mol % of Phenylsulphonate Ions Substituted for Bromide Ions.

diamagnetic anisotropy the doublet evolved from the inner peaks of the powder pattern. Each sample was observed under a polarizing microscope after concentration gradients had been set up by drying out the samples. The regions of low water concentrations next to the nematic region showed oily streaks and pseudo isotropic textures, characteristic of lamella structures. It was inferred all the samples of the amphiphilic nematic phases used in these studies had disk shaped micelles, i.e., there was no change in the micelle structure of the samples when the sign of the diamagnetic anisotropy changed. The spectrum width of the multiline proton nmr spectra of the phenyl sulphonate ion approximately doubled at the transition in diamagnetism. The spectra of two of the samples 10% and 50% on either side of the transition were analysed using the computer program. Known *J*'s were used and it was assumed the anisotropic part of *J* was equal to zero. The results of the computer analysis are presented in Table

IV. It was found the dipolar couplings at each side of the transition were of opposite sign. This infers the degree of orientation of the phenylsulphonate changed signs when the sign of the diamagnetic anisotropy changed, which is to be expected. Although the absolute sign and magnitude of S_{xx} and S_{zz} changed with the sign of the diamagnetism the ratio S_{xx}/S_{zz} in the two samples investigated were equal to -0.15 ± 0.01, i.e., constant within experimental error. This means the binding of the phenysulphonate does not change significantly as more phenyl sulphonate ions are introduced into the micelle surface. The phenylsulphonate ion does displace over the range under study about 10% of the solubilized decanol. The negative value for ratio S_{xx}/S_{zz} does mean the symmetry axis of the phenylsulphonate ion lies in the direction generally parallel to the micelle surface normal, tilted at an angle of less than 35° away from the normal. This angle is probably nearer to 35° than to zero because of the relatively small value of the ratio S_{xx}/S_{zz}. The diamagnetic anisotropy for hydrocarbon chains is negative, whereas for aromatic rings it is positive.[11] If the diamagnetism of the constituent molecules dominates the diamagnetic properties of the nematic phase and not the inherent shape diamagnetism of the micelle, increasing amounts of phenylsulphonate ion will make the diamagnetic anisotropy move through zero and end up positive, as was observed.

During the same situation the hydration of the micelle surface changes somewhat, where the D_2O ^2D quadrupolar splitting rose from 0 to 70 Hz. The binding D_2O to the micelle surface is not at all well understood whereas the binding of high symmetry ions are much better understood but binding of ions of lower symmetry have not been thoroughly investigated. A preliminary investigation has been made here where two separate studies have been made using a mixed detergent system.

The cationic detergents are alkyltrimethylammonium bromides with two different anionic detergents, potassium decanoate and *N*-decanoyl-alaninate (see Table II and III). The results for potassium decanoyl-alaninate are illustrated in Figure 2. There is no change in the sign of the dipolar coupling with either anionic detergent as would be expected. There were significant changes in the ratio D_{PA}/D_{HH} which were greater than the experimental error. The changes are too big to be assigned to structural distortion and are probably due to multisite ion binding where the first site has multi-coordination. The first site will have been partially destroyed by the introduction of the anionic detergent, while the second site will have been partially formed. Therefore the abrupt change in the sign of the dipolar coupling ob-

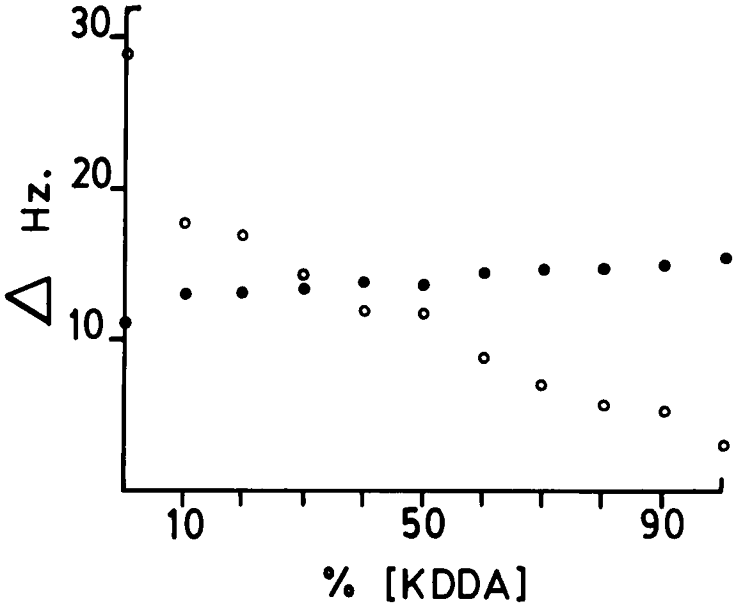

FIGURE 2 Absolute values of $3D_{HH}$ (○) and $2D_{HH} + J_{PH}$ (●) (Δ) from the proton nmr for the methyl phosphonate ion measured in a mixed amphiphilic nematic liquid crystal where the detergents are alkyltrimethylammonium bromide and potassium N-dodecanoyl-*dl*-alaninate (*dl*KDDA) as a function of the molar % of *dl*KDDA, in the total detergent.

served here is due to a change in the sign of the degree of orientation, associated with diamagnetic anisotropy and not with ion binding.

CONCLUSION

The inclusion of an aromatic counterion such as the phenylsulphonate ion into an amphiphilic nematic liquid crystal based on the cationic detergent tetradecyltrimethylammonium bromide induces a change in the sign of diamagnetic anisotropy at 25–26% molar substitution, but a possible thermodynamic change associated with micelle structure does not take place. The changes in the signs of the dipolar coupling in the aromatic phenyl sulphonate and the methyl phosphonate ion are due to changes in the degree of orientation corresponding to a sign change in the diamagnetic anisotropy. There is no sign change due to ion binding at the micelle surface, although a gradual change in the water binding is observed. When the orientation and the nature of the ion binding of small molecules or ions dissolve in an amphiphilic nematic liquid crystal where the micelle shape and the sign of the diamagnetic anisotropy is known, proton nmr could be used to determine the absolute sign of the J coupling constant.

References

1. G. R. Luckhurst, *Quart. Rev.*, **22**, 179 (1968).
2. .P. Diehl and C. L. Khetrapal, "NMR Basic Principles and Progress," Vol. 1, 1969 edited by D. P. Diehl, E. Fluck and R. Kosfield (Springer-Verlag).
3. R. C. Long and J. H. Goldstein, *Mol. Phys.*, **30**, 681 (1975).
4. N. Boden, K. Radley and M. C. Holmes, *Mol. Phys.*, **42**, 493 (1981).
5. N. Boden, P. H. Jackson, K. McMullen and M. C. Holmes, *Chem. Phys. Lett.* **65**, 476 (1979).
6. B. J. Forrest, L. W. Reeves and C. J. Robinson, *J. Phys. Chem.*, **85**, 3244 (1981).
7. A. S. Tracey and T. L. Boivin, *J. Phys. Chem.*, **88**, 1017 (1984).
8. A. S Tracey, *Can. J. Chem.*, **62**, 2161, (1984).
9. A. S. Tracey and K. Radley, *Mol. Cryst. Liq. Cryst.*, **122**, 77 (1985).
10. A. S. Tracey and K. Radley, *J. Phys. Chem.*, in press.
11. C. L. Khetrapal and A. C. Kunwar *Israel J. Chem.*, **23**, 299 (1983).
12. P. Diehl and J. Jokisouri, *Chem. Phys. Lett.*, **87**, 494 (1982).
13. K. Londsale, *Proc. R. Soc.* A, **171**, 514, (1939).