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G. A. Nagana Gowda^a; R. G. Weiss^{ab}; C. L. Khetrpal^a

^a Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India ^b Georgetown University, Washington, D.C., U.S.A.

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Silver nitrate-acetonitrile and iodine-benzene complexes as studied by NMR in thermotropic liquid crystals

by G. A. NAGANA GOWDA, R. G. WEISS† and C. L. KHETRAPAL*

Sophisticated Instruments Facility, Indian Institute of Science,
Bangalore 560 012, India

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Silver nitrate-acetonitrile and π iodine-benzene complexes in thermotropic liquid crystals have been studied by ^1H , ^2H , and ^{13}C NMR spectroscopy and by optical microscopy. Evidence for at least two silver complexes in each liquid crystal is presented.

1. Introduction

NMR investigations of weak complexes in thermotropic liquid crystals have been restricted thus far to Li^+ in lithium perchlorate [1, 2] and lithium tetra-fluoroborate [3] and to bromine-pyridine charge transfer complexes [4]. The former studies indicate formation of metal ion-solute as well as the metal ion-liquid crystal complexes. Evidence for the bromine-pyridine charge transfer complex derives from an increase of the order parameter along the C_2 axis of symmetry of pyridine, upon addition of bromine. Here, results on the formation of silver ion-solute complexes and iodine-benzene π complexes are reported. To the best of our knowledge, this is the first report on the study of a weak π complex in liquid-crystalline media using NMR [5].

2. Experimental

Silver nitrate (Sigma, 99 per cent), acetonitrile- d_3 (Aldrich, 99.8 per cent), iodine (Aldrich 99.99 per cent) and benzene (Analar grade, Ranbaxy, India) were used as received. Acetonitrile (Merck 99 per cent) was refluxed over phosphorus pentoxide for 5 h in a dry nitrogen atmosphere and distilled after 24 h. A centre fraction was collected. The liquid crystals, ZLI-1167 (a ternary eutectic mixture of propyl, pentyl and heptyl bicyclohexylcarbonitriles) and S-1114 (*trans*-4-pentyl-4'-(4-cyanophenyl)cyclohexane) from Merck were dried by heating at 120°C until the characteristic doublet in the proton spectra. All solutions were prepared under nitrogen atmosphere and in the presence of phosphorus pentoxide, in order to minimize contamination by moisture. Utmost care was taken in the preparation of the samples. The samples were vigorously mixed with a vortex stirrer in the isotropic phase before recording the spectra in the liquid-crystalline media. Solutions of acetonitrile in the liquid crystals were prepared and ^1H and ^2H NMR spectra recorded at various concentrations of silver nitrate. Spectra were also recorded between 18 and 63°C . Similarly, ^1H and ^{13}C NMR spectra of benzene were obtained in ZLI-1167 with and without various amounts of iodine. Proton spectra were recorded at 270 MHz on a Bruker WH-270 FT-NMR spectrometer equipped with an

* Author for correspondence.

† On sabbatical from Georgetown University, Washington, D.C., U.S.A.

ASPECT-2000 computer. ^2H and ^{13}C NMR spectra were obtained at 46.1 and 75.47 MHz on a Bruker MSL-300 FT-NMR spectrometer equipped with an ASPECT-3000 computer. About 10, 20 and 200 free induction decays were accumulated and Fourier transformed for the ^1H , ^2H and ^{13}C NMR spectra, respectively. Delays between the various scans in the spectra were empirically selected to allow complete relaxation of the spins. The limiting digital resolutions were 2, 12 and 6 Hz for the ^1H , ^2H , and ^{13}C NMR spectra, respectively. The optical textures of the various solutions were examined under a polarizing microscope fitted with a heating stage.

3. Results

^1H NMR spectra of acetonitrile in both liquid crystals show the normal 1:2:1 triplet arising from proton-proton dipolar couplings. Addition of about 1 wt.% silver nitrate to a solution of 4 wt.% acetonitrile in ZLI-1167 (sample A) led to a distinct separation of two phases. The ^1H NMR spectrum of the mixture shows an additional line near the centre of the triplet due to acetonitrile or an acetonitrile containing species in an isotropic-like environment. Visually, it is the bottom portion which appears isotropic-like. At 22°C, addition of more silver nitrate to sample A increases the triplet splitting from 4440 to 4800 Hz. Further addition of silver nitrate results in the appearance of a second triplet and disappearance of the isotropic-like singlet. Typical spectra of sample A and the mixture with 12 wt.% silver nitrate (referred to as sample B) are shown in figure 1.

As the temperature of sample B is increased, the splitting of the outer component decreases much more than that of the inner, leading to cross-over of the two triplets near 63°C. The top and bottom layers of sample B were separated and their ^1H NMR spectra recorded. The inner triplet at room temperature corresponds to acetonitrile from the bottom layer and the outer triplet arises from the upper layer.

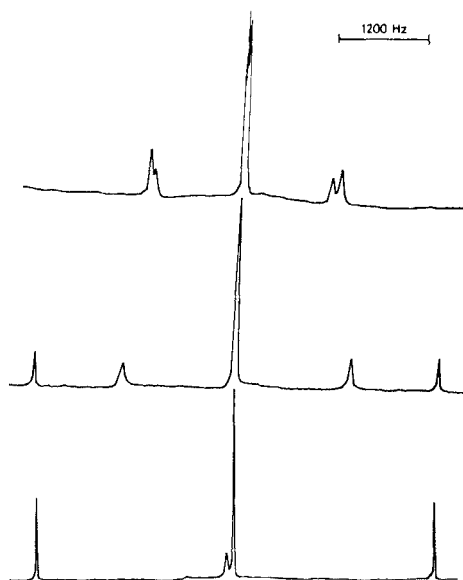


Figure 1. ^1H NMR spectra at 270 MHz of samples A and B. Lower trace is for sample A at 22°C; central and top traces are for sample B at 22 and 63°C, respectively.

^2H NMR spectra of acetonitrile- d_3 in both liquid crystals show essentially normal quadrupole split doublets with each component of the doublet exhibiting the fine structure due to deuterium–deuterium dipolar couplings typical of an oriented CD_3 group [5]. Addition of silver nitrate to acetonitrile- d_3 –ZLI-1167 solutions yields spectra which can be interpreted like the ^1H NMR spectra from samples A and B. Hence at 18°C , addition of 2 wt.% silver nitrate to 5 wt.% of acetonitrile- d_3 in ZLI-1167 (sample C) results in spectra containing a singlet near the centre of the doublet. Further addition of silver nitrate (up to about 7.4 wt.%) leads to no perceptible spectral changes except for an increase of the quadrupole splitting from 6150 to 6886 Hz. More silver nitrate (7.9 wt.%, referred to as sample D) leads to the appearance of a second quadrupole split doublet with fine structure due to deuterium–deuterium dipolar couplings. The separation between the outer and the inner components of the doublets are 6956 and 3294 Hz, respectively. The temperature dependent spectral changes are also analogous to those observed for sample B (i.e. as the temperature is increased the decrease in the splittings is much larger for the outer components than for the inner). Typical spectra are shown in figure 2. Optical microscopic studies of the individual layers of sample B reveal essentially similar textures that appear to be predominantly nematic with another anisotropic phase present in small amounts.

The ^1H and the ^2H NMR spectra of acetonitrile and acetonitrile- d_3 in S-1114 containing silver nitrate show the appearance of an oriented and isotropic-like species at all temperatures and concentrations examined. A typical spectrum is shown in figure 3. In this case too, a visual separation into two layers was observed with the lower portion appearing isotropic. The NMR spectrum of the lower layer provides the isotropic component and the upper one the spectrum expected for the oriented species. Polarizing microscopic studies of these samples reveal the existence of isotropic and nematic phases at all concentrations and temperatures with the lower layer being non-birefringent.

The ^1H NMR spectrum of a 2 wt.% solution of oriented benzene in ZLI-1167 (sample E) had a total width of 3884 Hz. An analysis of this spectrum using the

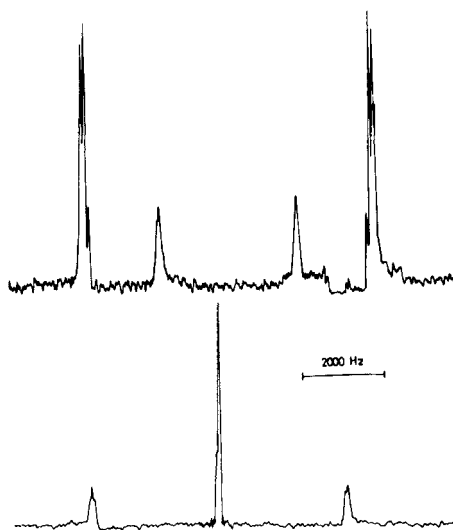


Figure 2. ^2H NMR spectra at 46.1 MHz of samples C and D at 18°C . Lower trace is for sample C; upper trace is for sample D.

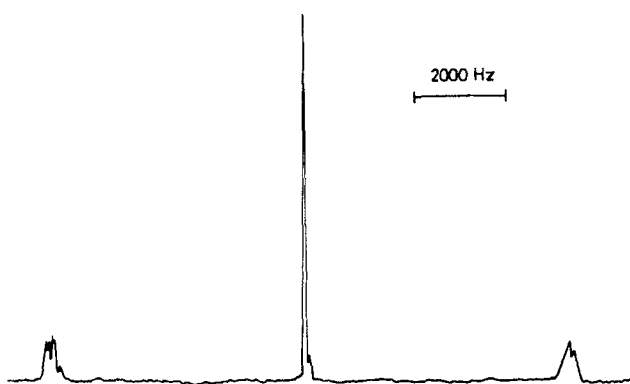


Figure 3. ^2H NMR spectra at 46.1 MHz and 18°C of 3 wt.% acetonitrile- d_3 in S-1114 containing 8.4 wt.% silver nitrate.

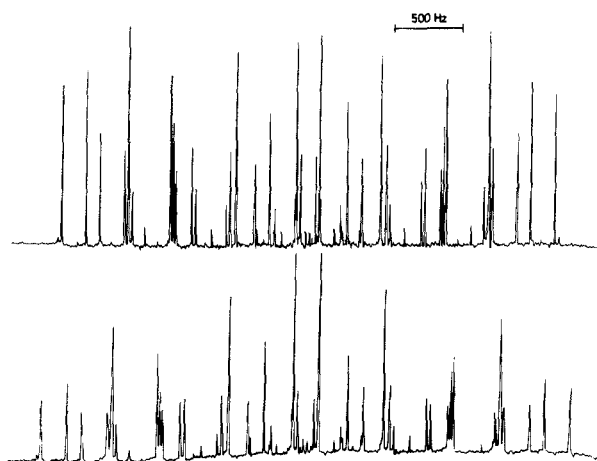


Figure 4. ^1H NMR spectra at 270 MHz of samples E and F at 22°C. Lower trace is for sample E; upper trace is for sample F.

LAOCONOOR programme [6] provides the interproton dipolar couplings between the ortho, meta and para protons (D_o , D_m , D_p respectively) as 514, 100 and 65 Hz, respectively. Addition of about 3.5 wt.% of iodine to this solution reduces the total spectral width to 3795 Hz. At 5.5 wt.% of iodine the spectral width becomes 3604 Hz (sample F) and $D_o=477$, $D_m=92$, and $D_p=60$ Hz. Typical spectra are shown in figure 4.

^{13}C NMR studies of the 2 wt.% solution of benzene in ZLI-1167 with and without iodine were also undertaken. The resonance from the benzene carbons was found to shift about 120 Hz down field upon the addition of about 3.5 wt.% of iodine; resonances from the nitrile carbons of ZLI-1167 were not shifted appreciably upon addition of iodine.

It may be emphasized that the change of the nitrile carbon chemical shift in ZLI-1167 is very sensitive to changes in the order parameter since the ^{13}C chemical shift anisotropy of the nitrile carbons is very large (352.2 p.p.m.) [3]. A change of 1 per cent of

the order parameter of the liquid crystal may result in the shift of the ^{13}C resonance to about 1.3 p.p.m. This implies insignificant change of the liquid crystal order upon addition of iodine.

4. Discussion

The observation of isotropic-like components in samples of $\text{CH}_3\text{CN}/\text{AgNO}_3$ in ZLI-1167 and S-1114 coupled with optical microscopic studies suggests a non-oriented environment irrespective of the nature of the acetonitrile containing species. At higher concentrations of silver nitrate in $\text{CH}_3\text{CN}/\text{AgNO}_3$ -ZLI-1167 samples (e.g. sample B), the disappearance of the isotropic component and the appearance of a second anisotropic component indicate that the silver complex with CH_3CN is present even at lower concentrations of silver nitrate (e.g. sample A). Silver complexes with ligands (L) such as CH_3CN are known to be linear (AgL_2), trigonal (AgL_3) and tetrahedral (AgL_4) [7]. It is also known that the silver complexes with acetonitrile are stronger than those with higher homologues or with aromatic nitriles [8]. The results, therefore, indicate the preferential formation of silver nitrate-acetonitrile complexes in these solutions. Therefore, the observation of spectra corresponding to the oriented species is consistent with ligated silver ions whose average distribution is non-tetrahedral (i.e. linear and/or trigonal).

The reduction of molecular order of benzene in ZLI-1167 upon addition of iodine as shown by the decreased proton spectral width is a fully expected consequence of the formation of a π complex between iodine and benzene [9]. From shape considerations, the order parameter of such a complex should be either opposite in sign to or smaller in magnitude than that of benzene under comparable conditions. The observed spectrum, which arises from the average orientation of the complexed and the free benzene will, therefore, have an order parameter which is smaller in magnitude than that of the uncomplexed benzene. The change of the chemical shift of the benzene carbons is consistent with this interpretation. Since the ^{13}C chemical shifts of the cyano carbons of ZLI-1167 do not change substantially, either the liquid crystal does not form a complex with iodine or the concentration of the complexed molecules is much lower than that of the uncomplexed. In either case, the order of the liquid-crystalline phase itself is not reduced appreciably by iodine.

5. Conclusions

NMR studies of acetonitrile in thermotropic liquid crystals containing silver nitrate indicate the formation of silver-acetonitrile complex(es). The spectra of the families of the species with one sample are distinct due to the complexes existing in separate layers. The formation of a π complex between iodine and benzene in ZLI-1167 is established from the reduction of the order parameter of the benzene protons as a result of the addition of iodine.

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