

# WEAK MOLECULAR INTERACTIONS: NMR SPECTROSCOPY OF ORIENTED MOLECULES

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## ABSTRACT

NMR spectroscopy of oriented molecules is employed to study weak molecular interactions. The information is obtained from the changes in the molecular order and the structure as a result of the complexation.

Specific results on the  $\pi$  and charge transfer complexes formed by iodine, chloroform, and silver nitrate with nitrogen heterocycles, aromatic systems and acetonitrile are reported. A method for the determination of the order parameter and the structure of the 'complexed' species is presented and its utility demonstrated. The use of mixture of liquid crystals of opposite diamagnetic anisotropies to investigate the extraordinary symmetry of Buckminster Fullerene,  $C_{60}$ , is illustrated.

## INTRODUCTION

Application of NMR to study weak molecular interactions from changes in chemical shifts, indirect spin-spin coupling constants and line width is quite well known and has been employed since the early days of NMR. However, the use of direct dipolar couplings/order parameters derived from the spectra of molecules oriented in thermotropic liquid crystals is relatively new (1) and provides more quantitative results since changes in molecular structure if any as a result of complexation

can also be determined directly and used for such a purpose.

Results on the  $\pi$  and the charge transfer complexes formed by chloroform, iodine, silver nitrate with aromatic systems, nitrogen heterocycles and acetonitrile are described in this communication. A study of Buckminster Fullerene ( $C_{60}$ ) oriented in mixture of liquid crystals of opposite diamagnetic anisotropies is also reported in order to establish the extraordinary symmetry of the molecule indicating, thereby, negligible solvent-solute interactions.

## 2. METHODOLOGY

Information on weak molecular complexes has been obtained from the changes in the degree of order as well as the molecular structure produced as a result of the complex formation.

The degree of order of a molecule dissolved in a nematic liquid crystal usually decreases with the increase of temperature or concentration. Any abnormal change in the degree of order is attributed to the formation of the complex(es). Recently, we have investigated metal ion ligand interactions between monovalent metal ions such as  $Li^+$  and  $Ag^+$  in  $LiClO_4$ ,  $LiBF_4$  and  $AgNO_3$  with ligands<sup>4</sup> like acetonitrile,<sup>3</sup> dimethyl sulphoxide, pyridine and acetone in thermotropic liquid crystals (2-4). Interactions of iodine (and bromine) with

pyridine (4-6), pyrimidine (7) and quinazoline (8) have also been investigated. Work on chloroform-benzene pi complexes has also been undertaken. We have also employed the use of mixture of liquid crystals of opposite diamagnetic anisotropies in order to find out if any detectable distortions in the spherical symmetry are present in Buckminster Fullerene,  $C_{60}$ , as result of solvent-solute interactions (9). Some such results are reported below briefly.

(a) LiClO<sub>4</sub>-ligand interactions: The ligands used in such studies are dimethylsulphoxide, acetonitrile and pyridine. The liquid crystals employed are Schiff bases such as N-(p-methoxy (or ethoxy) benzylidene)-p-n-butyl aniline (MBBA or EBBA) and their deuterated (-d<sub>2</sub>) analogue with deuterium substituted at position ortho to the -N= group in the butyl aniline ring. The results indicate the formation of two types of complexes in these cases with one having "isotropic-like" structure. The "isotropic-like" complex may be of the type ML<sub>4</sub> where M is the metal ion and L is the ligand and the other could be the one containing different ratios of the metal ions to ligands.

(b) LiBF<sub>4</sub>-Ligand solutions: The ligand used in such studies was acetonitrile. The liquid crystals employed were trans, trans-4-n-propyl (1,1'-bicyclohexyl)-4'-carbonitrile (ZLI-1184) and trans-4-pentyl-1-(4-cyanophenyl) cyclohexane (S-1114). The results indicate the formation of tetrahedral lithium-acetonitrile complexes and the coordination of lithium from LiBF<sub>4</sub> and LiClO<sub>4</sub> with the cyano group of ZLI-1184. No evidence was found to support either lithium ion complexation with S-1114 or the tetrafluorobo-

rate moiety in these systems.

(c) AgNO<sub>3</sub>-ligand complexes: In this case AgNO<sub>3</sub>-CH<sub>3</sub>CN (CD<sub>3</sub>CN) complexes have been investigated in two different liquid crystals, namely, ZLI-1167 (a ternary eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonitrile) and S-1114 from both the proton and the deuteron NMR studies. The results indicate the formation of different types of AgNO<sub>3</sub>-CH<sub>3</sub>CN complexes, i.e., ML<sub>4</sub>, ML<sub>3</sub>...etc.

(d) Benzene-chloroform complex: It has been studied from the reduction of molecular order of benzene upon addition of iodine. From the 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 of benzene in ZLI-1167 containing iodine which arises from the average orientation of the "complexed" and the "free" benzene, therefore, has an order parameter which is smaller in magnitude than that of the "uncomplexed" benzene. The change of the chemical shift of the benzene carbon is also consistent with this observation.

(e) Iodine(bromine)-pyridine charge transfer complex: Such complexes using NMR spectroscopy of oriented systems were first studied in 1973 and 1983 (5, 6) from the drastic change of the order parameter of the C<sub>2</sub>-axis of symmetry of pyridine. We have however, detected the formation of the "inner" complexes [(PYI)<sup>+</sup>I<sup>-</sup>] as well as those of the type PY.I<sub>2</sub> unambiguously. The order parameters of the "complexed" species have also been determined (4).

(f) Extraordinary symmetry of Buckminster Fullerene,  $C_{60}$  in nematic solutions: The  $^{13}C$ -NMR spectrum of  $C_{60}$  was studied in a mixture of nematic liquid crystals of opposite diamagnetic anisotropies. The method makes use of the change in the anisotropic parameters resulting from the switching of the order parameters at the critical point in the mixture; the change is by a factor of 2 or  $-1/2$  depending upon the direction of approach of the critical point (10). By an appropriate adjustment of the concentration and temperature, it is possible to observe both the types of orientations to coexist. Even in tetrahedral molecules such as methane and tetramethylsilane, the coexistence of the two spectra has been observed (11). On the other hand, the observation of a single line at the same position as in the isotropic phase at the critical point where the coexistence of the two spectra in methane or tetramethylsilane is observed, indicates the absence of any detectable distortions in the molecule. This has actually been observed in a solution of  $C_{60}$  in a 1:1 mixture of liquid crystals ZLI-1167 and S-1114 containing tetramethylsilane, at 332.4 K. The spectrum clearly shows the coexistence of two spectra for tetramethylsilane whereas for the  $C_{60}$  only a single line at its isotropic position (140.37 ppm with respect to TMS) is observed. The results, therefore, establish that there are no detectable distortions from spherical symmetry in  $C_{60}$  in the nematic solvents. To our knowledge this is the first molecule where no detectable distortion from spherical symmetry have been observed. It should, therefore, serve as an ideal reference for the study of the chemical shift anisotropy.

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