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Solvent–solute and solute–solute interactions from NMR in nematic phases

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The use of NMR spectroscopy of molecules oriented in liquid-crystalline media to study solvent–solute and solute–solute interactions in π-systems such as benzene–chloroform and in charge transfer complexes, for example pyridine–iodine, is illustrated. Changes in molecular order and chemical shifts as a result of complexation are employed in such studies. The extraordinary symmetry of C_{60} has also been investigated by using a mixture of liquid crystals of opposite diamagnetic anisotropies indicating, thereby, negligible solvent–solute/solute–solute interactions.

1. Introduction

The study of weak molecular complexes is important from both biological and chemical points of view. The use of NMR in this field, starting from the study of hydrogen bonding in simple alcohols to nucleic acids and the stacking interactions in proteins, has attracted the attention of numerous workers ever since the early days of NMR. The interactions are mostly investigated by the changes in chemical shifts, indirect spin–spin coupling constants, and/or the line widths as a result of formation/breaking of the complex(es). The use of nematic liquid crystals, both thermotropic and lyotropic, in such studies is, however, relatively new [1]. It makes use of changes in the molecular order/direct dipolar couplings or the structure/geometry as observed in such media due to complex formation/breaking. Results on benzene–chlorofom and pyridine–iodine are described in this communication. A method for studying minor distortions, if any, using mixtures of liquid crystals of opposite diamagnetic anisotropies [2, 3] is exploited to establish the extraordinary spherical symmetry in Buckminster Fullerene, C_{60}.

2. Experimental

Pyridine, benzene and chloroform, all AR grade, and iodine (Aldrich, 99·9 per cent) used in these studies were obtained commercially and further purified and dried before use. The C_{60} was prepared by the method reported in the literature [3]. The studies were undertaken using as solvent ZLI 1167 (a ternary eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonitrile) and S-1114 (*trans*-4-pentyl-1-4-cyanophenyl)cyclohexane). Utmost care was taken in the preparation of the samples and the purification of the solvents and solutes.

The spectra were recorded using Bruker WH-270 and AMX-400 spectrometers equipped with ASPECT-2000 and ASPECT-3000 along with X-32 computers, respectively. About 10 and 100 free induction decays were accumulated and Fourier transformed for the proton and the ^{13}C spectra for all the solutions except for the C_{60} compound for which nearly 25 000 scans had to be accumulated due to poor solubility.

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The spectra of the liquid crystal materials were first studied in order to ensure the purity of the solvents. The spectra of the liquid crystals containing chloroform and iodine were then studied in order to find out if any detectable complexation of chloroform/iodine occurred with the liquid crystal.

The proton spectra of about 2 wt% solutions of benzene and pyridine in ZLI 1167 were then recorded as functions of the concentrations of chloroform and iodine, respectively (see figures 1 and 2) at 298 K. The spectrum of pyridine itself was also studied as a function of concentration in ZLI 1167. Solutions containing 0·2 weight per cent of C_{60} and 4·2 weight per cent of tetramethylsilane in ZLI 1167, S-1114 and 1 : 1 mixtures of S-1114 and ZLI 1167 were studied at 323 and 358 K, i.e. in the nematic as well as isotropic phases, respectively. The mixture showed coexistence of the two types of spectra at 332·4 K (see figures 3 and 4).

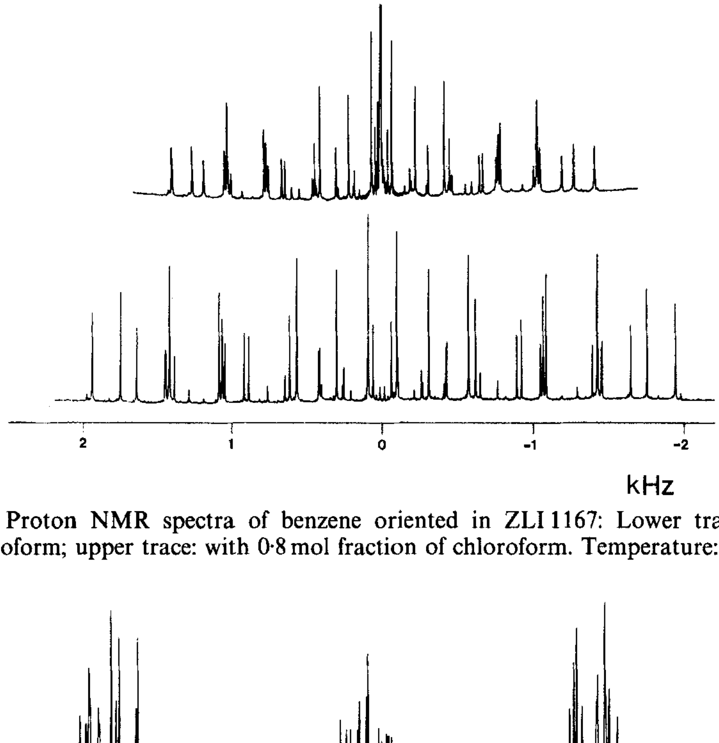

Figure 1. Proton NMR spectra of benzene oriented in ZLI 1167: Lower trace: without chloroform; upper trace: with 0·8 mol fraction of chloroform. Temperature: 298 K.

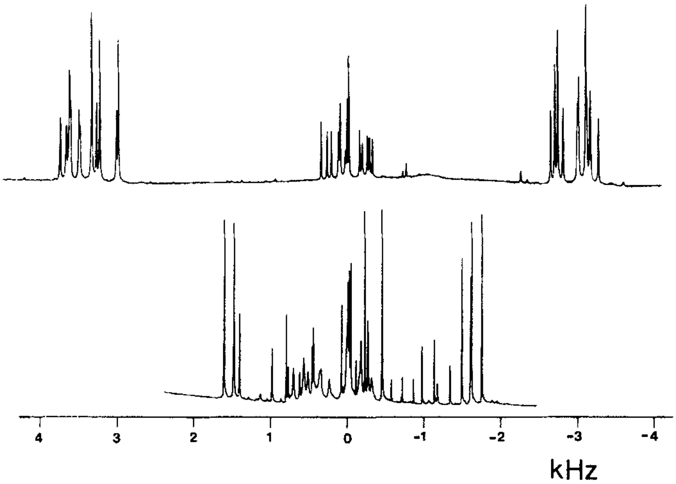

Figure 2. Proton NMR spectra of pyridine oriented in ZLI 1167: Lower trace: without iodine; upper trace: with 0·5 mol fraction of iodine. Temperature 298 K.

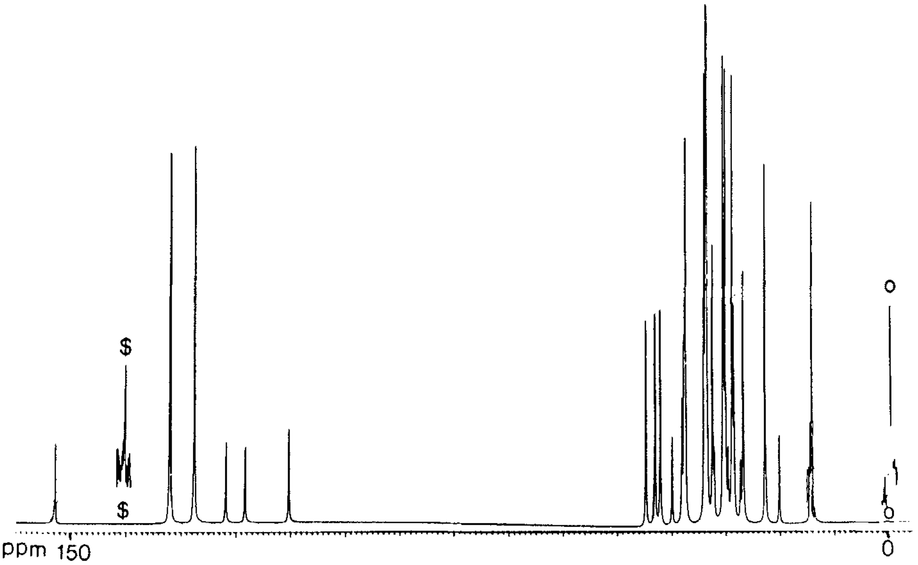

Figure 3. ${}^{13}C$ NMR spectra of 0·2 wt% of C_{60} containing 4·2 wt% of TMS in a 1 : 1 mixture of ZLI 1167: S-1114 at 358 K (isotropic phase). The line of C_{60} is indicated by ($) and that of TMS by (O). The lines due to C_{60} and TMS are also shown with a magnified vertical scale.

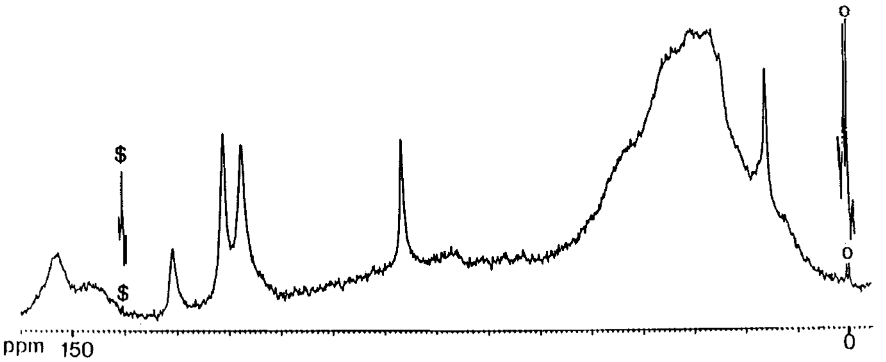

Figure 4. ${}^{13}C$ NMR spectra of the solution corresponding to figure 3 at 332·4 K (nematic phase). The coexistence of the two spectra is evident in the case of TMS.

3. Results of discussion

Information on weak molecular interactions has been obtained from the changes in the degree of order as a result of the complex formation. The degree of order of a molecule dissolved in a nematic liquid crystal usually decreases with increase in temperature or concentration. Any abnormal change in the degree of order is attributed to the formation of complex(es).

The ${}^{13}C$ spectra of the liquid crystal (ZLI 1167) with and without chloroform/iodine indicate that the ${}^{13}C$ chemical shift of the nitrile carbons in the liquid crystal does not change appreciably with addition of chloroform/iodine. On the other hand, the nitrile carbon chemical shift is very sensitive to changes in the order parameter, since the ${}^{13}C$ chemical shift anisotropy of these carbons is very large (352·2 p.p.m.). A change of 1 per cent in the order parameter may result in the shift of the ${}^{13}C$ resonance by more than 1 p.p.m. The fact that the nitrile carbons do not shift appreciably upon the addition of iodine or chloroform implies insignificant changes of the liquid crystal order upon addition of iodine or chloroform.

3.1. *Benzene–chloroform complex*

Figure 1 shows that the total spread of the spectrum for a 2 wt% solution of benzene in ZLI 1167 at 298 K changes from 3884 Hz to 2820 Hz for a solution containing 10 wt% chloroform under comparable conditions. An analysis of the spectra using known values of the indirect spin–spin couplings [4] provides the dipolar couplings between the *ortho-*, *meta-* and *para-*protons (D_o, D_m and D_p), respectively as 514·8, 89·9 and 65·1 Hz compared to 373·9, 72·5 and 47·3 Hz for the solution containing 10 wt% chloroform. The corresponding S_{xx} (in-plane order parameter) values change from −0·0655 to −0·0476. The reduction of the magnitude of the S_{xx} value of benzene upon addition of chloroform is a consequence of the formation of a π-complex between benzene and chloroform. This is also justified from considerations of the shapes of the 'complexed' and 'uncomplexed' species. The molecular dimension along the z axis (perpendicular to the plane) of the complex increases with the formation of the complex and this results in the decrease in the magnitude of S_{xx}.

3.2. *Iodine–pyridine charge transfer complex*

It may be seen from figure 2 that the spectra of pyridine in ZLI 1167 change drastically on addition of iodine. The spectra on addition of iodine reduce to 'deceptively simple' at higher iodine concentrations. This is due to the fact that the dipolar coupling D_{12} becomes predominantly large (see table). The results establish the formation of pyridine–iodine charge transfer complexes as concluded earlier [4, 5]. The fact that the spectra with and without iodine can be analysed by a single set of spectral parameters indicates that there is a rapid exchange between the 'complexed' and the 'uncomplexed' species and the average values of the parameters are obtained from the spectral analysis.

Spectral parameters of pyridine (with and without iodine) oriented in ZLI 1167.

	Value†	
Parameter	Without iodine	With 0·3 mol fraction of iodine
D_{12}	83·3 ± 0·5	876·2 ± 0·3
D_{13}	50·7 ± 0·1	140·4 ± 0·5
D_{14}	91·9 ± 0·5	48·7 ± 0·2
D_{15}	187·3 ± 0·2	42·3 ± 0·5
D_{23}	627·7 ± 0·1	350·1 ± 0·5
D_{24}	164·6 ± 0·2	35·6 ± 0·5
$\nu_1-\nu_2$	199·7 ± 0·3	308·3 ± 1·0
$\nu_1-\nu_3$	−147·5 ± 0·3	83·3 ± 1·0
S_{xx}‡	−0·1088	−0·0231
S_{yy}‡	−0·0104	−0·1096

Values of D_{ij} and $(\nu_i-\nu_j)$ are in Hz.

† The D values for a solution with 0·55 mol fraction of iodine are: $D_{12}=2088{\cdot}2$, $D_{13}+D_{23}=200{\cdot}6$, $D_{14}=-9{\cdot}2$, and $D_{24}+D_{15}=-344{\cdot}9$ Hz.

‡ S_{xx} and S_{yy} are the order parameters corresponding to the axes of the Cartesian coordinate system with x and y axes in the plane of the ring such that the y axis is the axis of C_2 symmetry.

The results indicate that the order parameters of pyridine in ZLI 1167 do not change appreciably as a function of concentration. Under the assumption that the order parameters S_{xx} and S_{yy} of pyridine do not change as a function of the solute concentration, it is possible to derive the order parameters of the 'complexed' species from equation (1)

$$(S_{ij})_E = X \cdot (S_{ij})_u + (1-X)(S_{ij})_c, \tag{1}$$

where $(S_{ij})_E$ is the experimentally derived order parameter of the axis ij and $(S_{ij})_u$ and $(S_{ij})_c$ are the corresponding order parameters of the 'uncomplexed' and the 'complexed' species respectively; X is the mol fraction of iodine. It may be mentioned that the error introduced in the estimation of the order parameters under such an assumption is about 10 per cent.

A plot of the $(S_{xx})_c$ and $(S_{yy})_c$ values against the concentration of iodine is shown in figure 5. The figure shows that the S_{xx} value first decreases and then increases as a function of the iodine concentration, and finally it becomes practically constant as the iodine concentration increases beyond 0·2 mol fraction. A reverse trend is observed for S_{yy}. The results unambiguously demonstrate that at least two types of complexes are formed for the pyridine–iodine systems. At lower concentrations of iodine, one type dominates and at higher iodine concentrations, it is the second type which is predominant.

A survey of the literature of pyridine–iodine molecular complexes [6–8] using various techniques shows the formation of various types of complex. At lower concentrations of iodine, the 'inner' complexes [$(PYI)^+I^-$) are essentially present, but at higher concentrations, $PY \cdot I_2$ type complexes are dominant. Though the formation of pyridine–iodine and pyridine–bromine complexes has also been reported earlier [4, 5] from NMR studies using nematic liquid crystal solvents, no evidence for the formation of more than one type of complex was obtained and it was not possible to estimate the order parameters of the 'complexed' species.

3.3. *Studies of Fullerene (C_{60})*

The carbon-13 NMR spectrum of C_{60} in CCl_4 solution shows a single line with an isotropic chemical shift of 142·5 p.p.m. down field of tetramethylsilane (TMS), establishing the equivalence of all 60 carbon atoms. In order to determine whether

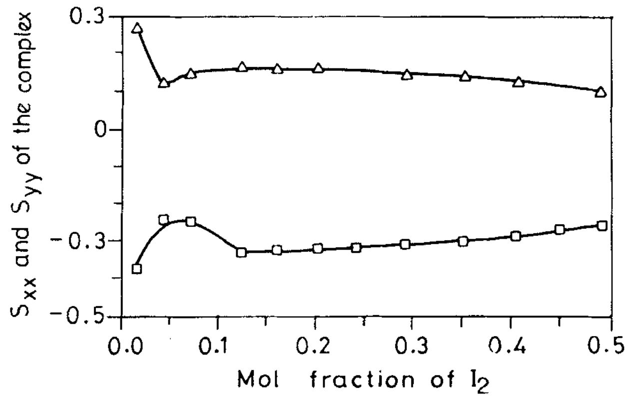

Figure 5. Variation of S_{xx} (△) and S_{yy} (□) of the charge transfer complex in the pyridine–iodine system as a function of the concentration of iodine.

slight distortions in the symmetry occur in the solution phase, a carbon-13 NMR spectrum of C_{60} was recorded using a mixture of nematic liquid crystals of opposite diamagnetic anisotropies. This method makes use of the change of the anisotropic parameters resulting from the switching of the order parameters at the critical point of the liquid crystal mixture; the change is by a factor of 2 or $-0{\cdot}5$ depending upon the direction of approach to the critical point. By a suitable adjustment of concentration and temperature, it is possible to achieve coexistence of both types of orientation. For tetrahedral molecules such as methane, such a coexistence of spectra, with shifts of nearly 0·5 p.p.m., has been observed. Observation of a single line near the critical point, at the same position as in the isotropic phase, would, therefore, indicate the absence of any detectable distortions [3].

Coexistence of two lines separated by 0·54 p.p.m. is clearly observed for TMS (see figure 4). This was stable for over a week while the sample was in the magnet, indicating the stability of experimental conditions; C_{60} on the other hand shows only a single sharp line at 140·37 p.p.m. with respect to TMS. This is exactly at the same position as in the spectrum in the isotropic phase (see figure 3). This shows that the product of the order parameter, S, and the chemical shift anisotropy, $\Delta\sigma$, is zero. $S=0$ implies an overall spherical symmetry of the molecule, while $\Delta\sigma=0$ shows local tetrahedral symmetry at each carbon site. The position of the ^{13}C signal at 140 p.p.m. is non-typical of tetrahedral symmetry and $\Delta\sigma$ is generally quite large for aromatic carbons (nearly 200 p.p.m. or more). The present results, therefore, correspond to $S=0$. To our knowledge, this is the first observation of a zero order parameter for a molecule dissolved in a liquid crystal. The observation of the zero value of the order parameter unambiguously corresponds to practically no distortions caused by the anisotropic pressure of the liquid crystal and/or vibrational–rotational effects.

4. Conclusions

NMR studies of oriented molecules provide a powerful technique for the study of weak molecular interactions. The information is obtained from the changes of the order parameters or changes of molecular structure as a result of the complexation.

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