Solute–Solute Interaction in Liquid Crystal Solvents: A Nuclear Magnetic Resonance Study of Pyridine–Iodine Molecular Complex in the Nematic Phase

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^{1}H N.m.r. spectra of [^{14}N]- and [^{15}N]-pyridine partially oriented in nematic phase IV in the presence of iodine show dipolar couplings (D_{ij}) increasing linearly as a function of iodine concentration. The spectral changes induced by iodine can be rationalized, to a first approximation, by assuming that the pyridine molecule is in equilibrium, in the oriented phase, with the pyridine–iodine charge transfer complex so that a considerable variation in the mean orientation of the pyridine moiety occurs. Attempts to reproduce the measured dipolar couplings of the exchanging complex on the basis of an average geometry and orientation afforded only dramatic distortion effects on the apparent geometry. Looking, moreover, at the geometry of [^{15}N]pyridine in phase IV and in other liquid crystals geometrical distortions were also found, probably due to solute–solvent interactions, except for the ZLI 1167 phase, where an r^{α} structure in close agreement with gas-phase microwave measurements was observed. The results suggest that, for pyridine in the nematic phase in the presence of iodine, at least a three-site mechanism is operating, one of the sites being the complexed pyridine.

Although the liquid crystal n.m.r. method has been widely applied to structure determination,[1,2] very few attempts have been made until now to detect the effect on the geometry and orientation parameters when a molecule is forming a molecular complex with another molecule, in the fluid solution of a nematic phase.[3]

The determination of molecular structures by n.m.r. in liquid crystal solvents is not an easy method to apply, as extensively discussed.[1,2] One of the problems arises from solute–solvent interactions. As shown for acetylene by the pioneering work of Diehl *et al.*,[4] there is, in some cases, the possibility of the formation of a complex between solute and solvent so that an equilibrium situation is created between free and complexed molecules. In all cases so far, for this two- or many-site mechanism, the rate of exchange between sites was fast with respect to the n.m.r. time scale, so that a unique spectrum was observed. However, since the dipolar couplings derived from the spectra of exchanging species are a complex function of orientations, geometries, and populations of the different sites, dramatic distortions may appear if we fit these couplings to a unique geometry and orientation.[4]

The determination of the order and the structure of molecular complexes is therefore expected to be very difficult, for not only is possible solute–solvent exchange present here but also solute–solute exchange. Since, however, in particular cases, a stable complex between solutes may be formed preferentially, the n.m.r. in liquid crystal solvents could in principle be very useful for studying molecular complexes in a liquid-like phase.

In this paper we report an n.m.r. investigation on the pyridine–iodine charge transfer complex partially oriented in a nematic phase. In a previous note [5] the degree of alignment of this complex was related to its shape, but it was not possible to obtain definite structural information because the spectra were poorly determined. Now, using [^{15}N]pyridine and obtaining ^{15}N satellites of the ^{1}H spectrum, we have, in principle, a sufficient number of couplings in order to tackle the structural problem. Moreover, as discussed before, in this kind of study it is necessary to assess also the influence of the solvent effect on the free ligands. Therefore a re-examination of the structure of [^{15}N]pyridine was carried out in a series of liquid crystal solvents and the structural results compared.

Experimental

The ^{1}H n.m.r. spectra of solutions containing 10 mol% [^{14}N]pyridine and quantities of iodine ranging from 0 to 60 mol% with respect to pyridine in nematic phase IV (Merck) were recorded at 30 °C, with a Varian XL 100 spectrometer in the Fourier transform mode using an external ^{19}F lock. Figure 1 shows some of the spectra. Greater quantities of iodine were not used in order to avoid perturbation of the solvent and a consequent change of the critical temperature.

An analogous experiment was performed with [^{15}N]pyridine, the other experimental conditions remaining the same. The partially oriented spectra of [^{15}N]pyridine in ZLI 1167 (Merck) (8% w/w) and in the nematic phase of 4,4′-di-n-heptylazoxybenzene (HAB) [6] (5 mol%) were also recorded using double wall tubes and D_2O for external deuterium lock. In the case of ZLI 1167, since this mesophase orients with the principal axis at right angles to the field, fast spinning was allowed and a mean linewidth of 1.5 Hz was obtained. An attempt to investigate the effect of iodine addition was made also for the ZLI 1167 solution. Unfortunately only a very small quantity of iodine dissolved in this solution, indicating that both iodine and pyridine–iodine complex are scarcely soluble in ZLI.

Spectral analysis of the partially oriented spectra was made by means of the LEQUOR program, taking the *J* values from the literature.[7] The dipolar couplings in ZLI 1167, HAB, and phase IV at zero iodine concentration are given in Table 1.

If the [^{14}N]- and [^{15}N]-pyridine D_{ij} couplings in phase IV are plotted against iodine concentration, they fit a linear trend with good correlation coefficients (*r ca.* 0.95). The D_{15} and D_{24} dipolar couplings for concentrations of iodine >20% start to become increasingly correlated so that only their sum was utilized in the treatment of data.

In Figure 2 the D_{ij} couplings of [^{15}N]pyridine *versus* iodine

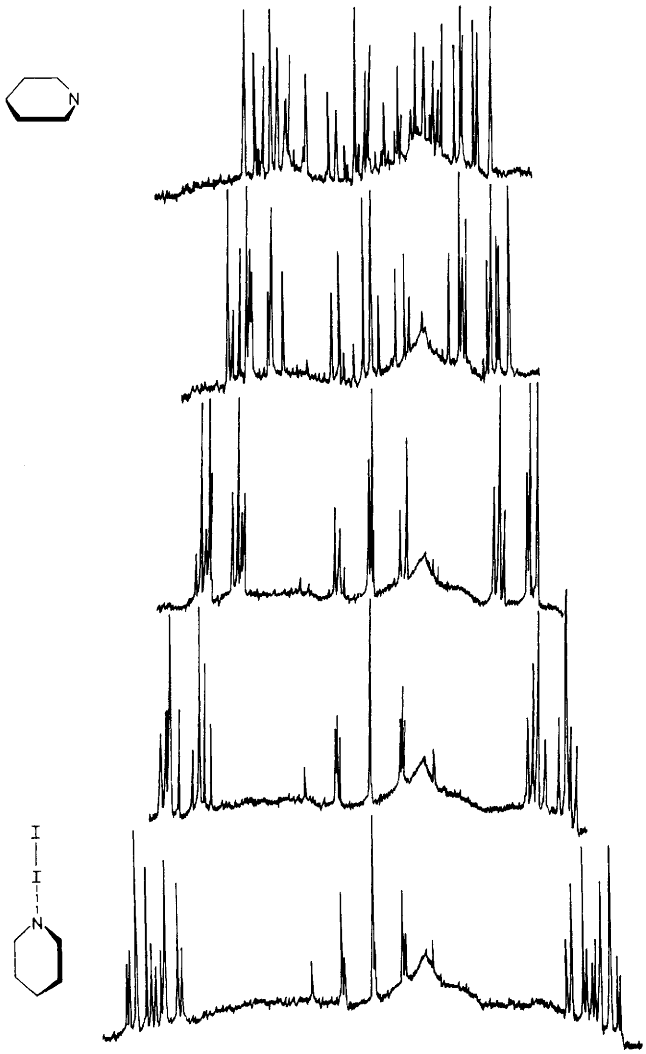

Figure 1. ^1H N.m.r. spectra of [^{14}N]pyridine in phase IV; the quantity of added I_2 increases from the top (0%) to the bottom (60 mol % with respect to pyridine). The axis of highest order degree is perpendicular to the ring for free pyridine, parallel to the N–I–I direction for the complex

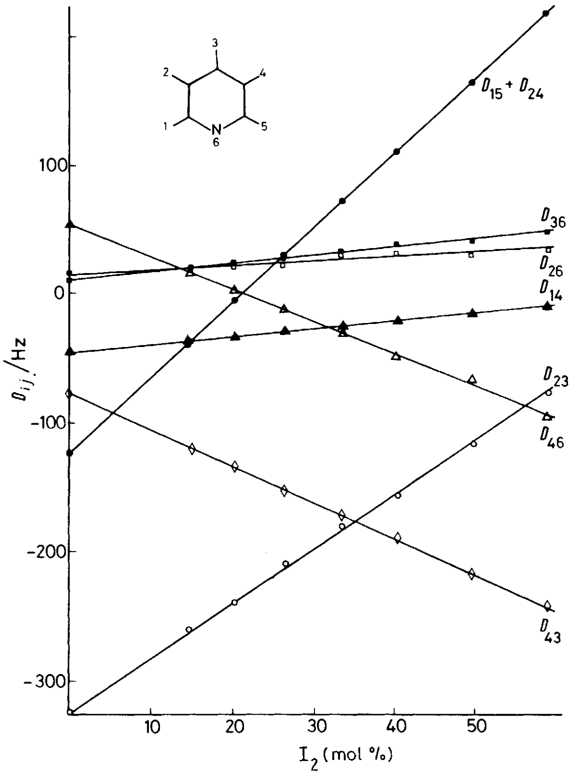

Figure 2. D_{ij} couplings of [^{15}N]pyridine *versus* I_2 concentration. D_{12} ranges from −418 Hz to −2724 Hz and cannot be plotted on this scale

concentration are shown as an example. In the last column of Table 1 the D_{ij} couplings of the [^{15}N]pyridine–iodine complex extrapolated at 100% I_2 concentration are also reported.

The experimental dipolar couplings, when used for structural investigations, were corrected for harmonic vibrations.[8] The corrections were computed suitably modifying the force field of benzene, given by Painter *et al.*,[9] in order to reproduce the experimental vibrational frequencies of pyridine.[10]

Results and Discussion

All the spectra of pyridine partially oriented in phase IV in the presence of iodine are reproduced by a unique set of averaged couplings. We can conclude, therefore, that the times of exchange between different molecular situations present in solution are faster than the inverse of the differences between the dipolar couplings of the individual species. It is also clear that in solution at least two species are present in equilibrium, namely pyridine complexed with iodine and free pyridine: the large increase in orientation along the *y* axis has in fact to be ascribed to the greater orientation which is expected for the pyridine–iodine complex along the same axis.

In order to test for the presence of a multi-site exchange we could plot the ratio r_{15}/r_{24} derived from $\sqrt[3]{D_{24}/D_{15}}$ as a function of I_2 concentration. Since r_{15} and r_{24} share the same direction, this ratio ought to be independent of the order parameters and constant if only one species were present. In the case of a two-site exchange, on the other hand, dramatic distortions in such a distance ratio are expected when the I_2 concentration and hence the mean orientation of the pyridine moiety is varied.

Unfortunately only the sum ($D_{15}+D_{24}$) is defined from the spectra for I_2 concentrations >20%, so that the ratio r_{15}/r_{24} is of little use for testing the multi-site exchange.

If, however, the spectra in the whole concentration range of I_2 are utilized to obtain a mean molecular geometry, with the help of the SHAPE computer program, very inconsistent results are found when compared with the geometry of pyridine as determined by microwave measurements[11] or by n.m.r. in ZLI 1167. On the other hand, looking at the results of Table 2, where the geometrical data for pyridine in various solvents and gas-phase microwave measurements are collected, we see that the results in phase IV (with no iodine added), are also quite different from those obtained in the gas phase or in ZLI 1167. The r^α structure in phase IV is by far the most distorted even if compared with the not well determined r^α structure in HAB or with the results in the fifth column of Table 2.[10]

A number of effects can be invoked when a molecular geometry obtained from n.m.r. in liquid crystal solutions appears distorted if compared with gas-phase data.[4,12,13] In the present case a two-site exchange could be present even for free pyridine in phase IV. Within this hypothesis, when iodine

Table 1. N.m.r. parameters for [^{15}N]pyridine

J_{ij}/Hz	Value [a]	D_{ij}/Hz	ZLI Exp. value [b]	HAB Exp. value	Phase IV Exp. value	Extrapolated values
1,2	4.97	1,2	103.46(7)	−295.0(1)	−418.6(1)	−2 724.2(10)
1,3	1.81	1,3	42.95(10)	−62.5(2)	−76.4(2)	−358.8(6)
1,4	0.9	1,4	62.34(7)	−48.8(2)	−43.9(1)	14.0(6)
1,5	−0.16	1,5	131.54(10)	−88.3(3)	−66.5(5)	
1,6	−10.06	1,6	−105.44(14)	69.9(2)	52.8(2)	−195.7(10)
2,3	7.83	2,3	451.86(7)	−364.7(1)	−325.8(2)	100.5(8)
2,4	1.38	2,4	114.72(14)	−77.3(3)	−58.1(5)	
2,6	−1.56	2,6	−12.46(20)	13.4(3)	15.2(2)	51.1(10)
3,6	0.18	3,6	−2.80(10)	8.0(3)	11.1(3)	76.0(6)
		$D_{15} + D_{24}$				454.8(1)
		$\nu_2 - \nu_1$	131.8(1)	140.9(4)		
		$\nu_3 - \nu_1$	82.8(1)	107.4(4)		

[a] Ref. 7. [b] Numbers in parentheses are standard deviations in units of the last digit quoted.

Table 2. Internuclear distance ratios and order parameters for [^{15}N]pyridine

r_{ij}/r_{23} [a]	r^{α} n.m.r. (ZLI)	r^{α} n.m.r. (HAB)	r^{α} n.m.r. (phase IV)	r^{α} n.m.r. [b]	r^{α} n.m.r. [c]	r^{s} MW [d]
1,2	0.990 9(15)	1.012(22)	0.938(6)	0.995(8)	0.995(20)	0.989(7)
1,3	1.707 7(17)	1.735(24)	1.653(7)	1.720(11)	1.721(13)	1.711(6)
1,4	1.947 0(5)	1.960(7)	1.965(2)	1.957(12)	1.951(17)	1.947(9)
1,5	1.638 4(3)	1.644(9)	1.699(5)	1.655(16)	1.646(10)	1.639(5)
1,6	0.820 1(3)	0.824(4)	0.851(2)	0.828(8)	0.825(5)	0.821(3)
2,4	1.716 5(6)	1.713(9)	1.754(5)	1.716(3)	1.711(9)	1.713(5)
2,6	1.337 9(70)	1.373(22)	1.319(5)	1.333(21)	1.352(17)	1.344(5)
3,6	1.536 3(90)	1.589(40)	1.466(12)	1.533(25)	1.565(8)	1.549(4)
S_{xx}	−0.077 40(3)	0.052 1(7)	0.043 2(4)	−0.140 9(25)		
S_{zz}	0.091 49(9)	−0.093 8(8)	−0.090 1(5)	−0.211 3(51)		

[a] The reference distance is r_{23} = 2.509 Å for this work, assumed by the r^{s} MW structure. [b] Results from the set of extrapolated dipolar couplings at 100% iodine concentration. [c] Ref. 10. Reference distance r_{23} = 2.492 Å for these ratios. [d] Ref. 11.

is added, a three-site equilibrium is possibly present and, since the temperature is constant, each dipolar coupling can be expressed as the sum of three terms [equation (1)] where C_1—

$$D_{ij} = C_1 S_1^{ij} G_1^{ij} + C_2 S_2^{ij} G_2^{ij} + C_3 S_3^{ij} G_3^{ij} \qquad (1)$$

C_3 are the equilibrium relative molar fractions of free pyridine, pyridine complexed with the solvent, and pyridine complexed with iodine, respectively, S_1^{ij}—S_3^{ij} are the orientation parameters of the molecule in the three sites, and G_1^{ij}—G_3^{ij} are functions of the geometry of pyridine in each site (*e.g.* $G_1^{ij} = -k_{ij}/r_{ij}^3$).

When some further assumptions are accepted, expression (1) nicely explains the linear dependence of all D_{ij} couplings on the total iodine concentration (C_{I_2}) displayed in Figure 2. First, the mesophase is supposed to be not severely perturbed by the iodine added and the order matrix of the pyridine moiety in each site is considered constant even when the population of the site varies. (As already pointed out, only iodine concentrations lower than 0.6 mol. equiv. of pyridine were used to avoid perturbing the mesophase.) It is also assumed that C_3 is in practice equal to C_{I_2}. Such a hypothesis is not unrealistic, since the complexation constant between the two molecules is generally high[14] and since an excess of pyridine with respect to iodine was used throughout.

With these approximations $C_1 + C_2 = C_{py} - C_{I_2}$, where C_{py} is the analytical concentration of pyridine. Moreover free and solvent-complexed pyridine are at equilibrium, so that $C_2/C_1 = K$. Combining the last two expressions we obtain equations (2) and (3). The linear dependence of the D_{ij} couplings on C_{I_2} directly follows.

$$C_1 = (C_{py} - C_{I_2})/(K + 1) \qquad (2)$$

$$C_2 = (C_{py} - C_{I_2})K/(K + 1) \qquad (3)$$

According to this interpretation and extrapolating the D_{ij} couplings to 100% iodine concentration, we obtain a set of D_{ij} values which are nothing but the dipolar couplings of the pyridine moiety in the pyridine–iodine complex. The extrapolated D_{ij} couplings are also shown in Table 1, while in Table 2 the distance ratios and the orientation parameters derived from these extrapolated couplings are displayed. The distance ratios for the pyridine–iodine complex thus obtained are in good agreement with microwave measurements; the geometry and microwave r^{s} structure of the complex, as also appears from Figure 3, differ only slightly as far as 1- and 5-H are concerned. These results, when compared with the highly distorted structure of pyridine in phase IV even when no iodine is added, suggest that complexation by iodine removes pyridine from exchange with the solvent, which is the main source of geometrical distortion in the absence of iodine. Of course, the multi-site mechanism is not the unique explanation of solvent-induced distortions, and correlation between reorientational and vibrational motions[12,13] could explain the different geometrical results between pyridine and pyridine–iodine complex: the heavier and much more oriented complex could, for instance, have a completely different motion in phase IV and hence correlation of motions different from that of free pyridine.

The fact that there is no dramatic difference between the complexed and uncomplexed molecule is also in agreement with previous measurements on charge-transfer complexes.[15]

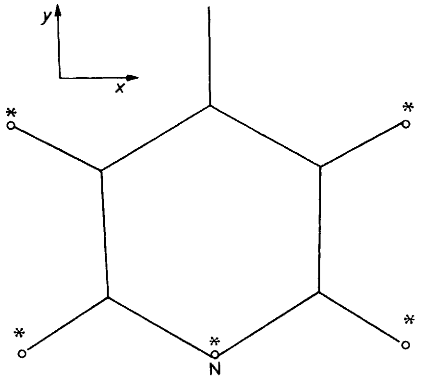

Figure 3. r^s Structure of pyridine (MW, ref. 11); on this scale it coincides with the r^α structure determined in ZLI 1167. Asterisks (*) and circles (○) define the r^α structure in phase IV for free and complexed pyridine respectively, the latter being obtained from extrapolated dipolar couplings. The origin of the reference frame is fixed on nucleus 3

On the other hand the theory of two- or many-site exchanges [4] does not require dramatic differences in geometry between complexed and uncomplexed species: the striking effects are due to amplification of small effects by orientation differences.

We conclude by observing that, although complexation by the solvent and solute–solvent interactions in general constitute a severe limit to the use of liquid crystal n.m.r. for the study of charge-transfer complexes, in particular cases, such as the present one of a strong complex between iodine and pyridine, the technique can give useful information concerning the shape, the structure, and the equilibria in the fluid phases.

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