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NMR of Bicyclic Diazines Oriented in a Lyotropic Mesophase

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Proton NMR spectra of bicyclic diazines such as phthalazine and quinoxaline have been studied in lyotropic liquid crystalline solvents. Values of the indirect spin–spin couplings which could not be derived from studies in the isotropic medium have been obtained. Geometrical information has been obtained in both the cases. The results are indicative of significant solvent–solute interactions in phthalazine but not in quinoxaline.

1 INTRODUCTION

Six membered ring systems with two nitrogens as heteroatoms occur widely in nature and play important roles in biological processes. Studies of the structure of such molecules is, therefore, important particularly in lyotropic solvents which serve as models for more complicated biological systems. They may provide useful information on solvent-solute interactions. A comparison of the geometrical data in thermotropic and lyotropic solvents using NMR spectroscopy has provided a novel method to study weak molecular interactions of the type involved in hydrogen-bonding, in monocyclic diazines like pyridazine.[1] It was, therefore, considered worthwhile to carry out investigations on bicyclic diazines to find out whether such interactions are present in relatively large bicyclic systems also. The results are reported in the present communication.

2 EXPERIMENTAL

Phthalazine and quinoxaline were commercially available. 2.3 and 2.9 weight per cent solutions of the compounds were made in the lyotropic phase formed by decyl ammonium chloride, heavy water, decanol ($-d_1$) and

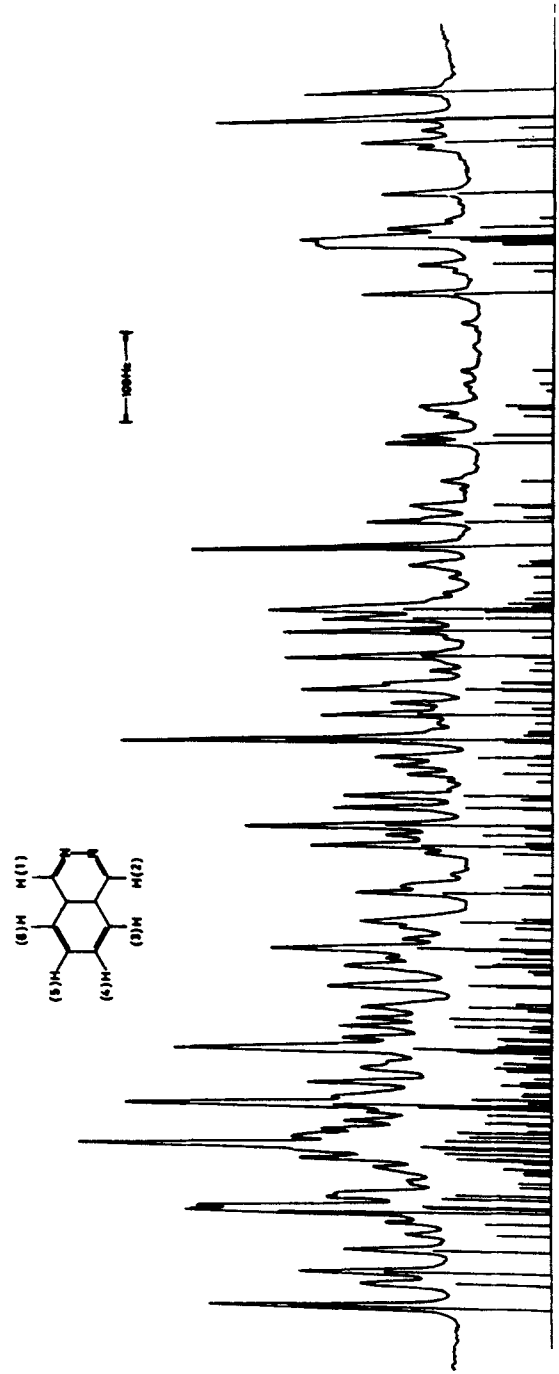


FIGURE 1 Observed and calculated proton NMR spectra at 20°C of 2.3 weight per cent phthalazine oriented in the lyotropic phase formed by decyl ammonium chloride, heavy water, decanol (d_1) and sodium sulphate. Spectrometer frequency is 270 MHz.

sodium sulphate. The phase is similar to that reported in the literature[2] except that ammonium chloride is replaced by sodium sulphate. Spectra were recorded at 20°C on a Bruker WH-270 FT-NMR spectrometer and 100 free induction decays were accumulated. Typical spectrum of phthalazine is shown in Figure 1.

The spectral spread was 1350 Hz for phthalazine and much larger (4750 Hz) for quinoxaline.

3 RESULTS AND DISCUSSION

3.1 Analysis of the spectra

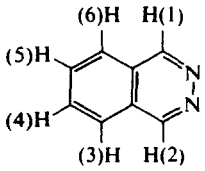
The spectra were analysed with the help of the LAOCOONOR program[3] on an IBM 360/44 computer. For phthalazine, the chemical shift ($\nu_i - \nu_j$) and the direct (D_{ij}'s) and the indirect (J_{ij}'s) spin-spin couplings were all iterated upon whereas for quinoxaline only J_{12} (Table I) was iteratively determined in addition to ($\nu_i - \nu_j$) and D_{ij}'s. In quinoxaline, iterations on the other indirect spin-spin couplings were not carried out since many lines in the spectrum overlapped with the solvent HDO peak and iterations on so many parameters would have reduced the accuracy. There was, however, a definite interest in iterating upon J_{12} in quinoxaline; a rather low value (1.7 Hz) for this coupling constant has been reported from the analysis of the ^{13}C-satellite spectrum of quinoxaline in the isotropic medium[4] and it was considered worthwhile to test this result. The parameters determined are reproduced in Table I. The value of J_{12} thus obtained is 0.9 ± 0.4 Hz. It is, therefore, certain that J_{12} in quinoxaline is much smaller than the coupling between ortho protons in benzenes. The table also shows that indirect couplings determined from present studies are in reasonable agreement with those obtained from investigations in isotropic and thermotropic solvents.[5,6] J_{12} in phthalazine which could not be determined from studies in the isotropic phase has been found as $\simeq 2$ Hz. It is larger than that for para protons in benzenes. The values for the corresponding indirect HH-coupling constants in pyrazine and pyridazine are 1.8[7,8] and 1.4[9] Hz respectively; they follow similar trends.

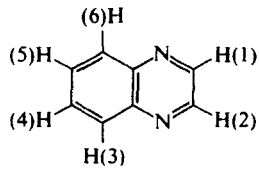
3.2 Molecular geometry

Of the nine HH direct dipolar couplings in phthalazine and quinoxaline, six are sufficient to define the shape of the proton skeleton and the two order parameters and hence the systems are over-determined by 3 coupling constants as far as the determination of molecular geometry and the order are

TABLE I

Spectral parameters in phthalazine and quinoxaline oriented in a lyotropic phase





Parameters	Phthalazine	Quinoxaline
J_{12}	2.07 ± 0.16 (−[c], 2.5 ± 0.5[b])	0.9 ± 0.4 (1.7[c])
J_{13}	0.35 ± 0.38 (0.4[c], 0.3 ± 0.2[b])	—
J_{14}	0.44 ± 0.29 (−, 1.0 ± 0.3[b])	—
J_{15}	0.13 ± 0.40 (−, −0.2 ± 0.1[b])	—
J_{16}	−0.31 ± 0.58 (−, −0.3 ± 0.2[b])	—
J_{34}	8.13 ± 0.19 (8.1[c], 8.9 ± 1.9[b])	8.4[a] (8.4[c])
J_{35}	0.97 ± 0.15 (1.2[c], 1.3 ± 0.3[b])	1.4[a] (1.4[c])
J_{36}	0.63 ± 0.20 (0.5[c], −0.1 ± 0.2[b])	0.6[a] (0.6[c])
J_{45}	6.95 ± 0.22 (6.7[c], 5.9 ± 0.4[b])	6.9[a] (6.9[c])
D_{12}	39.15 ± 0.06	−420.47 ± 0.14
D_{13}	22.45 ± 0.19	−63.97 ± 0.28
D_{14}	11.21 ± 0.21	−43.12 ± 0.23
D_{15}	12.46 ± 0.21	−56.84 ± 0.23
D_{16}	70.37 ± 0.29	−158.73 ± 0.27
D_{34}	132.69 ± 0.09	−888.79 ± 0.11
D_{35}	46.01 ± 0.10	−114.42 ± 0.12
D_{36}	35.93 ± 0.07	−55.31 ± 0.28
D_{45}	290.28 ± 0.10	−437.18 ± 0.30
$\nu_1 - \nu_3$	−383.15 ± 0.16	−271.88 ± 0.39
$\nu_1 - \nu_4$	−421.46 ± 0.14	−350.18 ± 0.37

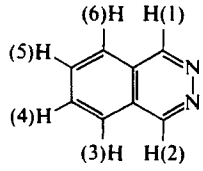
[a] assumed
[b] thermotropic values[5]
[c] isotropic values[6]

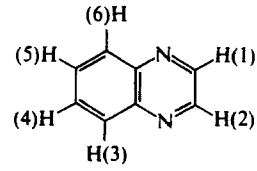
concerned. The least-square-fit programme SHAPE[10] was used to determine the "best-fit" geometrical and the order parameters. The values are reproduced in Table II. Those derived from studies in thermotropic solvents are also included (within parentheses) in the table for comparison.

It is seen from Table II that whereas the distance-ratios for quinoxaline derived from studies in lyotropic and thermotropic solvents[11] agree with each other, there are significant differences between the data for phthalazine. In fact, all the distance-ratios reported in Table II are smaller in the lyotropic solvent. A similar trend has been observed for pyrazine and pyridazine.[1] The deviation in the geometrical data obtained in thermotropic and lyotropic solvents for pyridazine has been attributed to a hydrogen bonded complex between the non-bonding electrons of the nitrogen atoms of the solute and

TABLE II

Geometrical and the order parameters in phthalazine and quinoxaline





Parameters	Value	
	Phthalazine	Quinoxaline
r_{12}/r_{45}	1.950 ± 0.002 (1.966 ± 0.013[a])	1.013 ± 0.001 (1.013 ± 0.002[a])
r_{14}/r_{45}	2.385 ± 0.020 (2.417 ± 0.012[a])	2.866 ± 0.060 (2.87 ± 0.04[a])
r_{34}/r_{45}	0.992 ± 0.007 (1.008 ± 0.004[a])	1.013 ± 0.009 (1.01 ± 0.02[a])
r_{35}/r_{45}	1.729 ± 0.005 (1.748 ± 0.005[a])	1.739 ± 0.009 (1.75 ± 0.02[a])
S_{xx}	−0.0095	0.1375
S_{yy}	−0.0369	0.0556
S_{zz}	0.0464	−0.1931

[a] Thermotropic values[5,11]. The indexing of the S-values is with respect to the Cartesian coordinate system such that the X and Y axes lie in the molecular plane with Y axis being parallel to the axis joining the nitrogen atoms.

the water of the lyotropic phase. A similar complex in phthalazine may explain the observed deviations.

3.3 Molecular orientation

Values of the order parameters and the coordinate system used are given in Table II. It is seen that the orientation parameters for the two systems are quite different. Magnitudes of the S-values are much larger in quinoxaline than in phthalazine. The largest positive S-value for phthalazine is along the Z-axis whereas for quinoxaline, S_{xx} is the largest positive and S_{zz} is negative. Such differences are also indicative of the solvent-solute interaction as discussed in section 3.2, in phthalazine.

4 CONCLUSIONS

The studies indicate that NMR spectroscopy of molecules oriented in different liquid crystals provide sensitive method to investigate weak molecular interactions and could be useful for studying interactions of small molecules with complicated biomolecules.

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