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NMR Spectra of Bicyclic Compounds Oriented in the Nematic Phase. Part 1. The Spectrum of Quinoxaline

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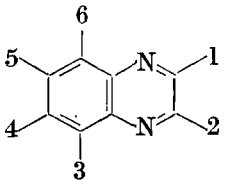
Abstract—The possibility of the determination of the structure of molecules oriented in the nematic phase of liquid crystals for relatively large aromatic bicyclic compounds is studied. The spectrum of quinoxaline is investigated in the nematic phase of 4-methoxy benzylidene, 4-amino-α-methyl cinnamic acid-*n*-propyl ester. The shape of the proton skeleton is iteratively determined. Values of some of the indirect spin spin coupling constants are determined.

The molecule is shown to orient preferentially with its plane and the C_2 axis along the direction of the magnetic field.

1. Introduction

The application of NMR spectroscopy of oriented molecules towards the determination of molecular structure has so far been restricted to small molecules and monocyclic aromatic systems[1] and no NMR data on the geometry of bicyclic aromatic systems are available. Some bicyclic systems can, however, be investigated as easily as the smaller molecules since the complexity of the spectrum depends only on the number of interacting nuclei. It opens interesting possibilities for the determination of molecular structure using the simple method of NMR spectroscopy in the liquid crystalline media.

In the present communication, the results on quinoxaline (I) oriented in a nematic phase are reported. The complete shape of the proton skeleton is determined.



(I)

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2. Experimental

Quinoxaline was commercially available and used without further purification. A 19.3 mole % solution of the compound in 4-methoxy benzylidene 4-amino-α-methyl cinnamic acid-*n*-propyl ester (a) was studied at 28 °C. The spectrum was recorded on a Varian HR-spectrometer at 56.445 MHz frequency. Several traces were taken and the average line positions were derived. Statistical error in the measurement of line position was 1.5 Hz. Average line width was 10 Hz.

3. Results and Discussion

3.1. Analysis of the Spectrum

The spectrum is shown in Fig. 1. Analysis was carried out with the help of the LACOONOR programme[2] which also contains the definitions of the coupling constants and the chemical shifts used in this paper. Values of the indirect couplings used were taken from the literature.[3] Iterative calculations were performed with both

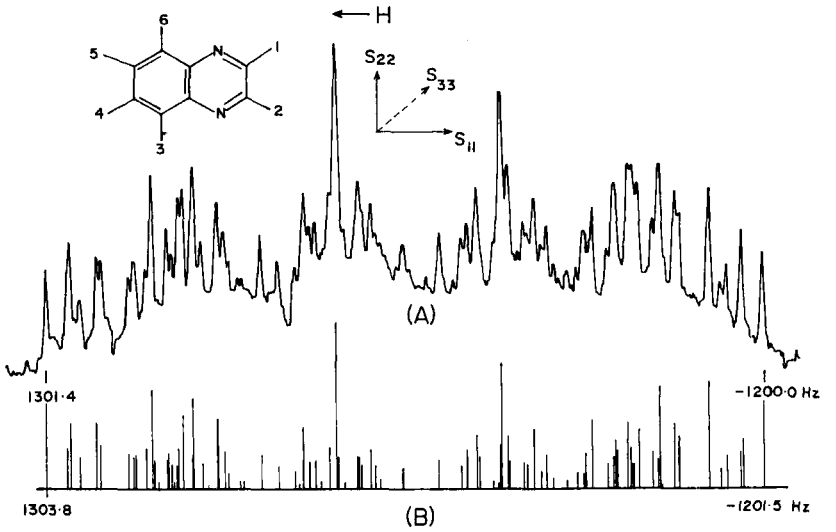

Figure 1. (A) observed and (B) calculated NMR spectra of quinoxaline oriented in the nematic phase (a). Concentration of the solute = 19.3 mole%. Temperature = 28 °C.

possible sign combinations of direct couplings (D) and the indirect couplings (J). An r.m.s. error of 1.5 Hz was obtained with the direct couplings having different signs from the indirect ones, and 3.3 Hz for the same sign of D's and J's. Thus, the signs of D's and J's must be opposite to each other. Since the signs of J's in substituted benzenes are positive, the direct couplings should have negative signs. They are reproduced in Table 1. Errors of the various parameters were determined as described earlier.[1] Iterations on the values of the indirect coupling constants were also done simultaneously with the D-values. It was observed that only J_{34} and J_{45} can be determined to a reasonable precision. The values were 7.7 and 6.9 Hz respectively (the literature values obtained from the NMR spectrum in the isotropic medium are 8.4 and 6.9 Hz respectively.[3]

3.2. Molecular Geometry

The quinoxaline molecule has a C_{2v}-symmetry and the proton skeleton is planar. There are nine independent coupling constants in the molecule and only two parameters suffice to describe the orientation. The system is over-determined as far as the determination, of the molecular geometry from the direct couplings is concerned. All the direct couplings could be determined reasonably accurately. Therefore, for the determination of the molecular geometry, the computer programme " SHAPE "[4] which calculates the geometry and the degree of orientation iteratively from its direct couplings,

Table 1 Values of the Parameters Obtained from the Spectrum of Quinoxaline Oriented in the Nematic Phase. The numbering of protons is given in Fig. 1

Parameter	Value (Hz)	Parameter	Value
D_{12}	-197.1 ± 0.2	r_{12}/r_{45}	1.013 ± 0.002
$D_{13} = D_{26}$	-42.7 ± 0.5	r_{13}/r_{45}	2.375 ± 0.05
$D_{14} = D_{25}$	-28.2 ± 0.2	r_{14}/r_{45}	2.87 ± 0.04
$D_{15} = D_{24}$	-38.4 ± 0.3	r_{15}/r_{45}	2.69 ± 0.04
$D_{16} = D_{23}$	-103.4 ± 0.5	r_{16}/r_{45}	1.89 ± 0.06
$D_{34} = D_{56}$	-573.1 ± 0.3	r_{34}/r_{45}	1.01 ± 0.02
$D_{35} = D_{46}$	-62.4 ± 0.2	r_{35}/r_{45}	1.75 ± 0.02
D_{36}	-25.7 ± 0.4	r_{36}/r_{45}	2.04 ± 0.02
D_{45}	-204.6 ± 0.3	S_{11}	0.094 ± 0.005
$\nu_3 - \nu_1$	46.5 ± 1.0	S_{22}	0.0260 ± 0.0001
$\nu_4 - \nu_1$	58.9 ± 0.9	S_{33}	-0.120

using weighted-least-square method, was used for the determination of the ratios of the interproton distances (Table 1). All the calculations were carried out on a CDC-3600 computer. The results indicate that the proton–proton distance in the pyrazine ring of the molecule is slightly larger than the corresponding distance in the phenyl ring which does not seem to distort from the normal benzene structure, within limits of experimental precision.

3.3. Molecular Orientation

The two S-values reported in Table 1 were determined with the help of the " SHAPE " programme and using $r_{45} = 2.481 \pm 0.005$ Å. The positive sign of S_{11} and S_{22} and the larger value of the former indicate that the preferred orientation of the molecule is with the magnetic field direction in the aromatic plane and along the C_2-axis of symmetry like other aromatics.[1]

4. Conclusion

The study broadens the field for the determination of molecular geometry from the NMR spectra in the liquid crystalline media and demonstrates that the method is applicable to relatively large bicyclic aromatic compounds.

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