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NMR Spectra of Bicyclic Compounds Oriented in the Nematic Phase.
Part II. The Spectrum of Phthalazine

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Abstract—The determination of the structure of molecules oriented in the nematic phase of liquid crystals for relatively large bicyclic aromatic compounds has been extended to phthalazine. The spectrum of the molecule is investigated in the nematic phase of a mixture of 80% 4-ethoxybenzylidene-4-*n*-butyl aniline and 20% *o*-carbobutoxy-4-oxybenzoic acid ethoxy phenyl ester. Values of the indirect spin-spin coupling constants are determined.

The geometry of the proton skeleton of the molecule is iteratively computed. The phenyl part of the molecule has been found to be distorted compared to the benzene structure. The distance between the protons in the pyridazine part of the ring is found to be smaller than the para H-H distance in the phenyl part.

The Molecule orients preferentially with its C_2-axis parallel to the direction of the magnetic field ($S_{c_2} = 0.1864$). The axis normal to the plane has the most negative S-value (-0.1703).

1. Introduction

Information on the geometry of relatively large bicyclic compounds, using various techniques is quite scarcely available in the literature. On the other hand, the use of the simple technique of NMR spectroscopy of oriented molecules towards the elucidation of the structure of such molecules has earlier been suggested and applied

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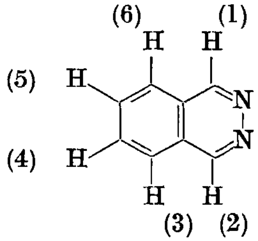
to the molecule quinoxaline.⁽¹⁾ The shape of the proton skeleton of the molecule has been determined and it has been found that (i) the proton skeleton of the phenyl part of the molecule is slightly distorted outside the limits of experimental accuracy; (ii) the H-H distance in the fused pyrazine ring is larger than the corresponding value in the phenyl ring, and (iii) the preferred orientation of the molecule resembles that of other aromatics. The molecule is preferentially oriented with the aromatic plane and the C_2-axis parallel to the magnetic field direction.

In the present investigation, the method has been extended to another bicyclic compound namely phthalazine (I). Geometry of the proton skeleton is determined and information about the molecular orientation derived.



(I)

2. Experimental

The sample of phthalazine used was commercially available. A 12 mole percent solution of the compound was prepared in a mixture of 80% 4-ethoxybenzylidene-4-*n*-butyl aniline (a) and 20% *o*-carbobutoxy-4-oxybenzoic acid ethoxyphenyl ester (b). The freshly prepared solution gave a spectrum of the dissolved compound with rather broad lines (width ≃ 35 Hz). The sample (in the 5 mm NMR sample tube) was then stored at about 28 °C for a few days in the horizontal position before the final spectrum with an average line-width of 6 Hz could be obtained.

The spectrum was recorded at 28 °C on a Varian XL-100 spectrometer† with the most intense line in the lowest field band of the

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spectrum providing the lock-signal. The complete spectrum was run in three parts with different sweep off-set readings. The sweep-width and the sweep time for each part were 2500 Hz and 2500 sec. respectively.

The error in the measurement of line position was 1.3 Hz.

3. Results and Discussions

3.1. ANALYSIS OF THE SPECTRUM

The spectrum of the compound is shown in Fig. 1.

It was analyzed iteratively using the LAOCOONOR program⁽²⁾ on a B-5500 computer. Calculations were carried out such that the chemical shifts ($\nu_i - \nu_j$) and the direct dipolar coupling constants (D_{ij}) were iterated upon and the values of the indirect spin-spin couplings (J_{ij}) were taken from the literature.⁽³⁾ An rms error between the observed and the calculated line positions was found to be 1.2 Hz; the values of D_{ij} and the relative signs of D_{ij} and J_{ij} obtained by this procedure are reported in Table 1. Since the ortho and the meta indirect couplings in benzenes are known to have positive signs, the absolute signs of direct couplings are as given in Table 1. Errors of the parameters were determined as described earlier.⁽⁴⁾

In addition, an iterative analysis of the spectrum was also made in which all the parameters including the indirect coupling constants were iterated upon. The last column of Table 1 reports the values of the indirect spin-spin coupling constants (J_{ij}) thus determined. The coupling constants determined from the spectrum in an isotropic solvent⁽³⁾ are included within parentheses in the same column of the table for comparison. The differences between the values of the indirect coupling constants obtained from the spectrum in the nematic phase and the ones in the isotropic medium are less than 1 Hz for all the coupling constants which could be derived from the isotropic spectrum. It may be mentioned that the precision of determination of some of the D-values decreases when all the parameters are derived from the spectrum in the nematic phase. Therefore, the values of the direct couplings in Table 1 obtained using the known values of the indirect couplings, were used for the determination of the geometry reported in Sec. 3.2. It may also be mentioned,

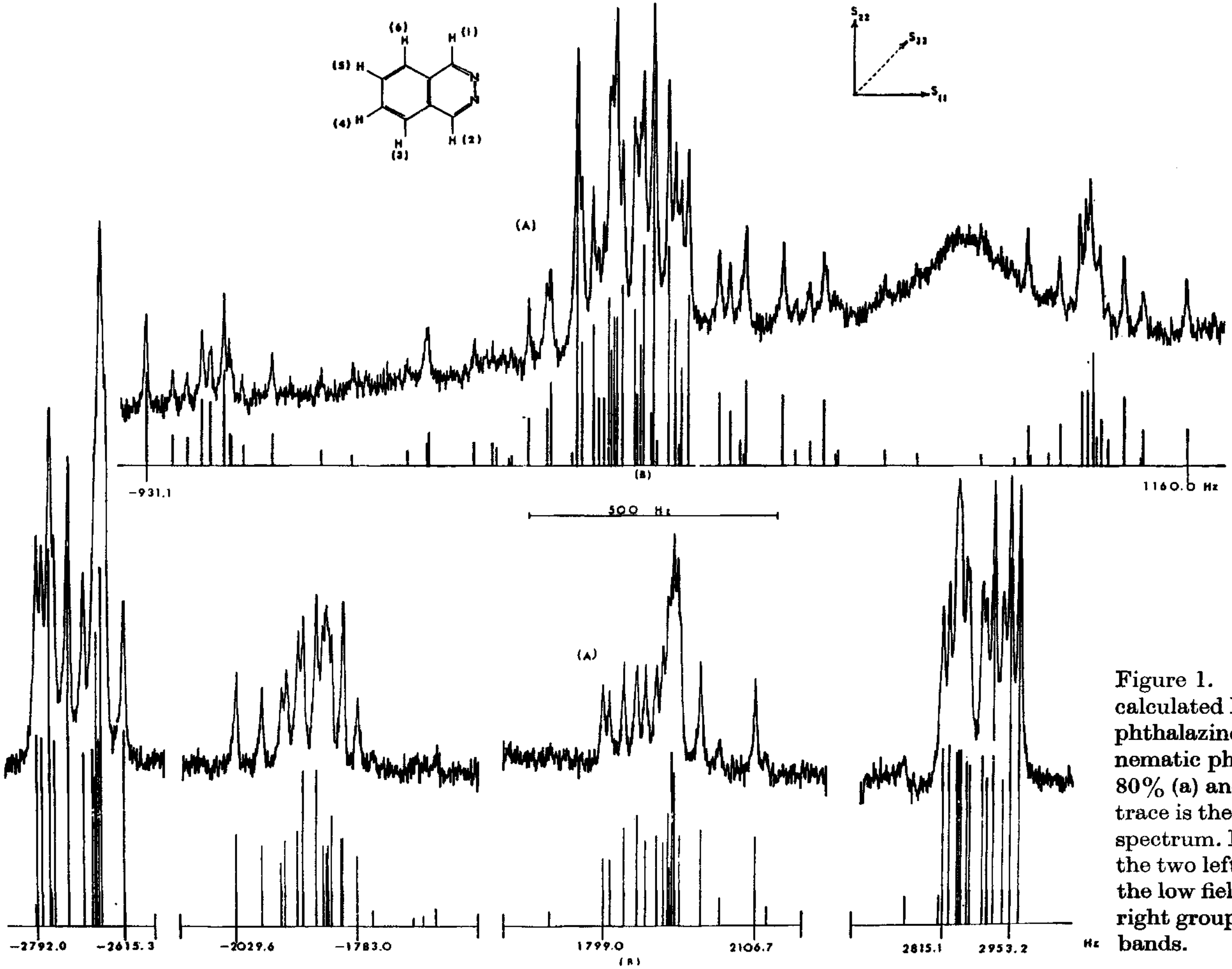

Figure 1. (A) observed and (B) calculated NMR spectra of phthalazine oriented in the nematic phase of a mixture of 80% (a) and 20% (b). The upper trace is the central portion of the spectrum. In the lower traces, the two left groups of lines are the low field bands and the two right groups are the high field bands.

TABLE 1 Direct Couplings, Chemical Shifts and Indirect Couplings Obtained for Phthalazine Oriented in the Nematic Phase of 80% (a) and 20% (b). The numbering of protons is given in Fig. 1.

Parameter	Value (Hz)	Parameter	Value† (Hz)
D_{12}	16.4 ± 0.2	J_{12}	2.5 ± 0.5 (—)
$D_{13} = D_{26}$	-18.9 ± 0.3	$J_{13} = J_{26}$	0.3 ± 0.2 (0.4)
$D_{14} = D_{25}$	-61.4 ± 0.1	$J_{14} = J_{25}$	1.0 ± 0.3 (—)
$D_{15} = D_{24}$	-179.3 ± 0.5	$J_{15} = J_{24}$	-0.2 ± 0.1 (—)
$D_{16} = D_{23}$	-1279.1 ± 0.9	$J_{16} = J_{23}$	-0.3 ± 0.2 (—)
$D_{34} = D_{56}$	-1019.0 ± 0.5	$J_{34} = J_{56}$	8.9 ± 1.9 (8.17)
$D_{35} = D_{46}$	-49.1 ± 0.1	$J_{35} = J_{46}$	1.3 ± 0.3 (1.24)
D_{36}	15.1 ± 0.2	J_{36}	-0.1 ± 0.2 (0.57)
D_{45}	126.2 ± 0.8	J_{45}	5.9 ± 0.4 (6.76)
$\nu_1 - \nu_4$	-129.1 ± 0.6	$\nu_3 - \nu_4$	20.1 ± 0.3

† Values in the parentheses are obtained from the spectrum in an isotropic solvent.(3) (—) indicates that the value from the spectrum in the isotropic medium is not reported.

that the values of the direct coupling constants obtained with and without iterations on the J-values did not differ outside their experimental errors, and hence the geometry information derived from the two sets of D-values is essentially the same.

3.2. MOLECULAR GEOMETRY

There are nine different direct couplings in the molecule phthalazine. Only six of these are needed to define the two order-parameters and the shape of the proton skeleton of the molecule. The system is overdetermined as far as the determination of molecular geometry from the direct dipolar coupling constants is concerned. The molecular structure was, therefore, determined with the help of an iterative procedure which computes the geometry and the degree of order from the determined direct dipolar couplings using a " weighted least-square " method.

The computer program " SHAPE "(5) was used for these calculations and all the coupling constants were given equal weights. Values of the direct couplings corresponding to the " best-fit " geometry are given in Table 2 together with the ratios of the H-H

TABLE 2 Direct Dipolar Coupling Constants Calculated for the "Best-Fit" Geometry, Ratios of the H-H Distances and the Order-Parameters in Phthalazin Oriented in the Nematic Phase of 80% (a) and 20% (b).

D-values calculated for the "best" geometry		Ratios of the H-H distances		Other parameters
D_{ij}	Value† (Hz)	r_{ij}/r_{45}	Values	
D_{12}	16.6 (16.4 ±0.2)	r_{12}/r_{45}	1.966 ±0.013	$r_{45} = 2.481 \pm 0.005$ (assumed) Å
$D_{13} = D_{26}$	−18.6 (−18.9 ±0.3)	r_{13}/r_{45}	2.258 ±0.015	$S_{11} = 0.1864 \pm 0.0033$
$D_{14} = D_{25}$	−61.3 (−61.4 ±0.1)	r_{14}/r_{45}	2.417 ±0.012	$S_{22} = -0.0161 \pm 0.0002$
$D_{15} = D_{24}$	−179.3 (−179.3 ±0.5)	r_{15}/r_{45}	1.969 ±0.011	$S_{33} = -0.1703$
$D_{16} = D_{23}$	−1279.1 (−1279.1 ±0.9)	r_{16}/r_{45}	1.046 ±0.015	
$D_{34} = D_{56}$	−1019.0 (−1019.0 ±0.5)	r_{34}/r_{45}	1.008 ±0.004	
$D_{35} = D_{46}$	−49.2 (−49.1 ±0.1)	r_{35}/r_{45}	1.748 ±0.005	
D_{45}	126.2 (126.2 ±0.8)	r_{36}/r_{45}	2.038 ±0.013	
D_{36}	14.9 (15.1 ±0.2)			

† Values within parentheses in this column are the experimental values.

distances and the order-parameters. The direct couplings experimentally determined are also included in Table 2 (within parentheses), for ready comparison.

Table 2 indicates that the differences between the observed and the calculated values of the direct couplings are within experimental errors. The results establish the planar structure of the proton skeleton and confirm the C_{2v}-symmetry of the molecule.

The results (Table 2) suggest that the phenyl part of the phthalazine molecule is distorted from the normal benzene structure (where $r_{34}/r_{45} = 1.000$, $r_{35}/r_{45} = 1.732$, $r_{36}/r_{45} = 2.000$ compared to 1.008 ± 0.004, 1.748 ± 0.005 and 2.038 ± 0.013 respectively in Table 2). In the quinoxaline molecule, the phenyl part of the molecule was found to be similarly distorted but the accuracy of determination of the parameters was relatively low in that case.

The proton-proton distance (r_{12}) in the pyridazine ring of the molecule seems to be shorter than the para H-H distance in the phenyl ring ($r_{12}/r_{36} = 0.973 \pm 0.008$ as determined directly from D_{12}

and D_{36}). In the quinoxaline molecule, the proton-proton distance in the pyrazine ring has been found to be slightly larger than the corresponding distance in the phenyl ring.⁽¹⁾ These results are well compatible with those obtained for pyrazine⁽⁶⁾ and pyridazine⁽⁷⁾ where similar distortions were found.

3.3. Molecular Orientation

The two order-parameters reported in Table 2 have been determined with the help of the " SHAPE " program and an assumed value of $r_{45} = 2.481 \pm 0.005$ Å. The positive sign and the magnitude of S_{11} are in agreement with what one would expect from the molecular shape which predicts that the largest S-value corresponds to the largest molecular dimension.

In another experiment using 4-methoxy benzylidene 4-amino-α-methyl cinnamic acid -*n*-propyl ester as the solvent, it has been found that the S_{11}-value is about the same. This value is approximately twice the one obtained for quinoxaline under comparable conditions. Since these two molecules have similar shape, it indicates that the position of the nitrogen atoms has an influence on the orientation that is not connected with the molecular shape.

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