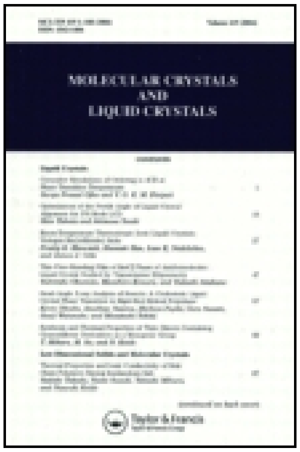

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NMR Investigations on Di- and Tri-Azanaphthalenes Oriented in Liquid Crystals

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NMR Investigations on Di- and Tri-Azanaphthalenes Oriented in Liquid Crystals

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Proton NMR spectra of 1,3-diazanaphthalene and 1,2,4-triazanaphthalene have been investigated in the nematic phase of three liquid crystals. The spectral analysis provided direct dipole–dipole couplings which have been used to derive the molecular structure. Geometry of the phenyl ring in both the molecules deviates from the regular hexagonal structure. Signs of the order parameter of the largest magnitude are opposite in liquid crystals with positive and negative diamagnetic anisotropies.

1. INTRODUCTION

In earlier publications,[1,2] we have reported results on phthalazine (1,4-diazanaphthalene) and quinoxaline (2,3-diazanaphthalene) oriented in nematic solvents. These are bicyclic systems containing a phenyl ring fused to pyrazine or pyridazine. The results on the bicyclic system formed by fusion of a phenyl ring with pyrimidine (1,3-diazanaphthalene) are reported in the present paper along with studies on another bicyclic compound containing a phenyl ring fused to a

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6-membered ring with 3 nitrogen heteroatoms (1,2,4-triazanaphthalene). This permits the evaluation of the distortions in the relative interproton distances as a result of substitution of nitrogen(s) in the ring. Furthermore, in order to derive more reliable information, studies in three different liquid crystal solvents have been undertaken and the combined geometrical data derived.

2. EXPERIMENTAL

The nematic phases of *N*-(*p*′-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) (I), Merck phase V (a mixture of *p*-*n*-butyl-*p*′-methoxyazoxybenzene and *p*-ethyl-*p*′-methoxyazoxybenzene) (II) and ZLI-1167 (a ternary eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonitrile) (III) were used as the solvents. The solute concentrations (in weight per cent) for the diaza and the triaza compounds were 3.0, 3.6 and 4.1, and 5.1, 6.1 and 4.4 in the liquid crystals (I), (II) and (III) respectively. The spectra were recorded at 19(±1)°C. One hundred free induction decays were accumulated for all the spectra on a Bruker WH-270 FT-NMR spectrometer. The Fourier transformation was performed on the 16K computer memory of the dedicated BNC-12 computer. Typical spectra of 1,3-diazanaphthalene and 1,2,4-triazanaphthalene in (I) are shown in Figures 1 and 2 respectively. Spectral line-widths varied from 4 Hz to 20 Hz though the lines were in general sharper in (III). The differential line broadening arises

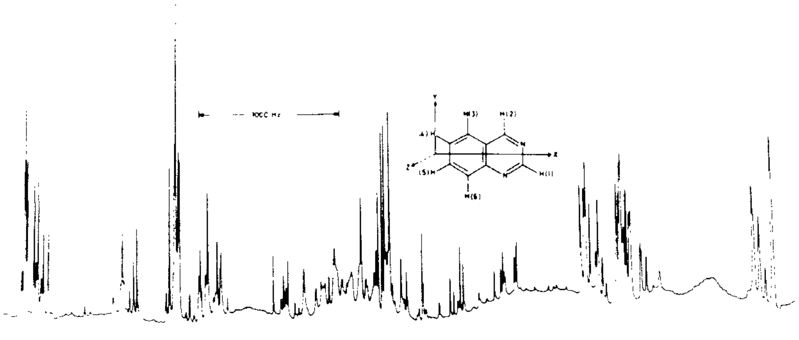

FIGURE 1 Proton magnetic resonance spectrum of 1,3-diazanaphthalene oriented in the nematic phase of MBBA.

Solute concentration:	3.0 weight per cent
Temperature:	19 °C
Spectrometer frequency:	270 MHz.

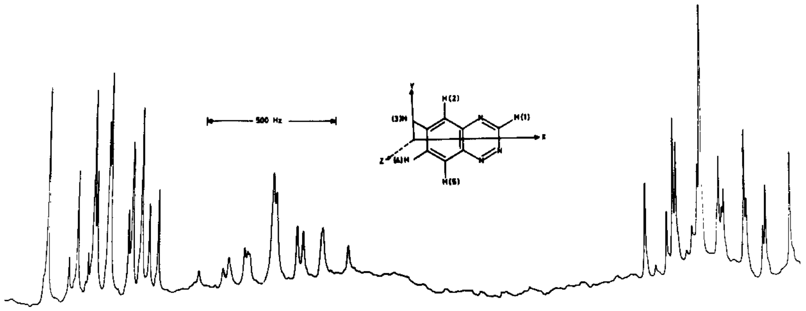

FIGURE 2 Proton magnetic resonance spectrum of 1,2,4-triazanaphthalene oriented in the nematic phase of MBBA.

Solute concentration:	5.1 weight per cent
Temperature:	19 °C
Spectrometer frequency:	270 MHz.

because of the quadrupolar relaxation of the ^{14}N nuclei. The broadening is more pronounced for the transitions essentially arising from the proton(s) in the ring containing the hetero nitrogen atoms. Similar differential line-broadening has been noticed in 2-fluoropyridine.[3]

3. SPECTRAL ANALYSIS

The spectra were analysed with the help of the LAOCOONOR programme[4] on a DEC-1090 computer. For 1,3-diazanaphthalene, the indirect spin–spin coupling constants (J_{ij}'s) were taken from the literature[5] and were not varied during the analysis. For 1,2,4-triazanaphthalene, the indirect spin–spin couplings are not available from studies in isotropic media hence the relevant values of 1,3-diazanaphthalene were used; small deviations in these values if any, do not influence the derived information outside the experimental error. In the final analysis for 1,3-diazanaphthalene where the chemical shifts ($\nu_i - \nu_j$'s) and the dipolar coupling (D_{ij}'s) were varied, 105 lines were fitted to a root-mean-square (rms) error of 1.09 Hz in (I), 164 lines were assigned to an rms error 0.90 Hz in (II) and 184 lines with the error of 0.66 Hz in (III). The derived spectral parameters are given in table I. For 1,2,4-triazanaphthalene, in the final analysis, 57 lines were assigned to an rms error of 0.45 Hz in (I), 61 lines were fitted with an rms error of 1.07 Hz in (II) and 77 lines to the error of 0.63 Hz in (III). Errors of the parameters given in Tables I and II are the probable errors provided by the LAOCOONOR programme.

TABLE I

Spectral Parameters[a] (in Hz) for 1,3-diazanaphthalene in MBBA (I), Merck Phase V (II) and ZLI-1167 (III). (Numbering of the Protons is given in Figure 1).

Parameter	In MBBA	In Merck Phase V	In ZLI-1167
D_{12}	-42.73 ± 0.19	-57.14 ± 0.18	92.13 ± 0.10
D_{13}	-58.84 ± 0.16	-75.25 ± 0.12	68.10 ± 0.10
D_{14}	-50.04 ± 0.16	-65.29 ± 0.15	51.62 ± 0.07
D_{15}	-71.11 ± 0.27	-91.26 ± 0.19	66.23 ± 0.13
D_{16}	-183.69 ± 0.27	-237.53 ± 0.20	169.32 ± 0.16
D_{23}	-1203.37 ± 0.23	-1546.38 ± 0.24	1127.02 ± 0.11
D_{24}	-163.23 ± 0.25	-211.01 ± 0.16	148.96 ± 0.21
D_{25}	-52.18 ± 0.39	-69.76 ± 0.30	49.34 ± 0.44
D_{26}	-13.14 ± 0.42	-19.77 ± 0.35	22.75 ± 0.42
D_{34}	-897.19 ± 0.36	-1173.54 ± 0.32	823.37 ± 0.26
D_{35}	-37.99 ± 0.56	-53.50 ± 0.52	51.64 ± 0.49
D_{36}	19.27 ± 0.53	17.72 ± 0.49	12.31 ± 0.45
D_{45}	138.41 ± 0.44	143.44 ± 0.38	82.51 ± 0.30
D_{46}	-49.40 ± 0.47	-64.62 ± 0.40	90.09 ± 0.28
D_{56}	-959.47 ± 0.10	-1226.46 ± 0.09	1018.14 ± 0.06
$\nu_2 - \nu_1^b$	83.92 ± 0.40	81.31 ± 0.29	-99.40 ± 0.29
$\nu_3 - \nu_1^b$	448.22 ± 0.26	429.57 ± 0.21	342.56 ± 0.22
$\nu_4 - \nu_1^b$	462.50 ± 0.30	441.69 ± 0.26	478.68 ± 0.14
$\nu_5 - \nu_1^b$	383.44 ± 0.51	355.66 ± 0.47	402.32 ± 0.44
$\nu_6 - \nu_1^b$	381.62 ± 0.51	378.71 ± 0.47	346.84 ± 0.43

[a] Indirect spin-spin coupling constants are[5]: $J_{26} = 0.5$, $J_{34} = 8.23$, $J_{35} = 1.37$, $J_{36} = 0.63$, $J_{45} = 7.03$, $J_{46} = 0.89$, $J_{56} = 8.59$ Hz: others have been taken as zero.

[b] At 270 MHz.

It should be pointed out that some of the parameters could not be determined accurately. A look at the variance-covariance matrix of the iterated parameters shows that the covariances of certain coupling constants and chemical shifts are relatively large. For example in 1,2,4-triazanaphthalene in (I), D_{12} and D_{13} are interdependent and in (II) ν_4 and ν_5 have strong dependence on each other. This accounts for the large errors of some of the parameters specially in Table II.

4. RESULTS AND DISCUSSION

Each of the molecules 1,2,4-triazanaphthalene and 1,3-diazanaphthalene possesses one plane of symmetry (namely the molecular plane) and hence needs 3 parameters for the specification of molecular orientation.

TABLE II

Spectral parameters[a] (in Hz) for 1,2,4-triazanaphthalene in the nematic phase of MBBA (I), Merck Phase V (II) and ZLI-1167 (III) (Numbering of the protons is given in Figure 2)

Parameter	In MBBA	In Merck Phase V	In ZLI-1167
D_{12}	−133.24 ± 1.29	−233.61 ± 0.41	204.33 ± 0.31
D_{13}	−59.11 ± 1.35	−94.76 ± 0.41	86.70 ± 0.31
D_{14}	−43.94 ± 0.22	−75.32 ± 0.66	68.02 ± 0.26
D_{15}	−55.60 ± 0.23	−94.67 ± 0.76	84.63 ± 0.26
D_{23}	−805.62 ± 0.08	−1373.36 ± 0.17	1245.44 ± 0.09
D_{24}	−60.14 ± 0.52	−104.40 ± 1.26	56.99 ± 0.57
D_{25}	−9.25 ± 0.59	−5.33 ± 1.23	−38.98 ± 0.29
D_{34}	−68.05 ± 0.43	−43.25 ± 1.35	−336.91 ± 0.21
D_{35}	−56.75 ± 0.74	−73.38 ± 1.32	2.75 ± 0.42
D_{45}	−714.68 ± 0.25	−1205.90 ± 0.31	948.38 ± 0.08
$\nu_2 - \nu_1^b$	564.02 ± 0.90	592.15 ± 1.48	444.02 ± 0.41
$\nu_3 - \nu_1^b$	572.01 ± 1.00	550.96 ± 1.59	496.86 ± 0.42
$\nu_4 - \nu_1^b$	609.52 ± 1.21	562.20 ± 3.32	544.56 ± 0.52
$\nu_5 - \nu_1^b$	396.09 ± 1.22	419.06 ± 3.31	358.06 ± 0.54

[a] Indirect spin–spin couplings used have been taken from that for 1,3-diazanaphthalene[5]: $J_{12} = 0.5$, $J_{23} = 8.59$, $J_{24} = 0.89$, $J_{25} = 0.63$, $J_{35} = 1.37$ and $J_{45} = 8.23$ Hz; others have been taken as zero.

[b] At 270 MHz.

For 1,2,4-triazanaphthalene ten independent dipolar couplings are obtained from each spectrum. Six ratios of the interproton distances required to fix the relative proton positions and the three order parameters needed to specify the molecular orientation can be determined from the 10 dipolar couplings derived from each experiment. However, since the system is overdetermined by just one coupling constant as far as the determination of the relative interproton distances and the order parameters from the dipolar couplings obtained from a single experiment is concerned, the derived values may not be accurate especially when there are relatively large uncertainties in some of the obtained coupling constants. A study in three different solvents provides 30 dipolar couplings from which 6 relative interproton distances and the 9 order parameters (3 for each experiment) can be determined to a much larger degree of confidence. The inherent assumption in such studies is, however, either the absence of the solvent effects on the molecular geometry and/or the presence of similar magnitudes of such effects for each experiment. This is reasonable for the systems of the type as those under investigation.[6] A modified version of the SHAPE programme[7] was used to derive the best fit structural and orientational parameters. The internuclear dis-

TABLE III

Ratios of the interproton distances in 1,2,4-triazanaphthalene. (For numbering of the protons, see Figure 2)

Parameter	Value
r_{12}/r_{34}	1.909 ± 0.006
r_{15}/r_{34}	2.330 ± 0.007
r_{23}/r_{34}	1.013 ± 0.002
r_{25}/r_{34}	2.055 ± 0.006
r_{35}/r_{34}	1.757 ± 0.002
r_{45}/r_{34}	1.026 ± 0.003

tances ratios are given in Table III. They were obtained by giving the weights to the dipolar couplings as the inverse of their errors given in Table II.

For 1,3-diazanaphthalene, 8 relative proton-proton distances and the 3-order parameters can be derived from the 15 dipolar couplings obtained from each experiment. However, for the sake of uniformity and for obtaining more reliable values, the 8 independent ratios of the interproton distances required to fix the relative proton positions and the 9 order parameters were determined from the 45 dipolar couplings obtained from the experiments in 3 different liquid crystals, in a manner analogous to that reported for 1,2,4-triazanaphthalene. The values are reported in Table IV. The table also includes the distance ratios for the 'model geometry' obtained by the fusion of the benzene

TABLE IV

Ratios of the interproton distances in 1,3-diazanaphthalene. (For numbering of the protons, see Figure 1).

Parameter	Value		
	This work	'Model Geometry'	X-ray data
r_{12}/r_{45}	1.654 ± 0.002	1.665	1.660
r_{16}/r_{45}	1.859 ± 0.003	1.844	1.860
r_{23}/r_{45}	1.031 ± 0.001	1.032	1.005
r_{26}/r_{45}	2.241 ± 0.003	2.229	2.231
r_{34}/r_{45}	1.003 ± 0.001	1.000	1.018
r_{36}/r_{45}	2.023 ± 0.002	2.000	2.012
r_{46}/r_{45}	1.738 ± 0.001	1.732	1.738
r_{56}/r_{45}	1.005 ± 0.001	1.000	1.001

and pyrimidine rings and the use of the corresponding values of the bond lengths and bond angles.[8,9] The geometrical data derived from X-ray diffraction studies[10] using the C—H bond length as 1.10 Å are also reported in the table for comparison.

The results (Tables III and IV) show that the phenyl ring deviates significantly from the regular hexagonal geometry like in phthalazine[1] and quinoxaline.[2] The distortions are larger for the triaza compound due to the presence of an additional nitrogen atom in the ring. In fact r_{25}/r_{34} is the largest (2.055) in 1,2,4-triazanaphthalene compared to the corresponding value in the diaza compounds (the values are 2.04, 2.038, 2.023 for phthalazine, quinoxaline and 1,3-diazanaphthalene, respectively).

The order parameters for both the molecules are given in Table V with respect to the Cartesian coordinate system defined in the table. The S_{xx} values have the largest magnitude and their signs are opposite for the solvents with positive and negative diamagnetic anisotropies. This behaviour is analogous to that for other aromatic compounds. The principal axes of the orientation tensor deviate by less than 3° with respect to the Cartesian coordinate system chosen for both the molecules in all the liquid crystals.

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TABLE V

Independent order parameters in 1,2,4-triazanaphthalene and 1,3-diazanaphthalene

		Value		
Compound	Parameter	In (I)	In (II)	In (III)
1,2,4-triazanaphthalene	S_{xx}[a]	0.1365	0.2348	−0.2166
	S_{yy}	0.0086	0.0055	0.0429
	S_{xy}	0.0067	0.0126	−0.0234
1,3-diazanaphthalene	S_{xx}[b]	0.1677	0.2154	−0.1565
	S_{yy}	−0.0176	−0.0184	−0.0107
	S_{xy}	−0.0034	−0.0023	−0.0135

[a] with respect to a right handed Cartesian coordinate system with X, Y axes in the molecular plane. The positive Y-axis joins proton 4 to 3. r_{34} = 2.481 A° (assumed) (Figure 2).

[b] With respect to a right handed Cartesian coordinate system with X, Y axes in the molecular plane. The positive Y-axis joins protons 5 to 4. r_{45} = 2.481 A° (assumed) (Figure 1).

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