

## Liquid Crystal Nuclear Magnetic Resonance Investigation on the Structure of a Molecule formed by Two Fused Six-membered Rings: 2,7-Naphthyridine

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The n.m.r. spectrum of the 2,7-naphthyridine partially oriented in the nematic phase of a liquid crystalline solvent has been obtained and interpreted in terms of chemical shifts, spin-spin coupling constants, and direct dipolar couplings. The ratio of the interprotonic distances has been deduced and the molecular shape obtained. Comparison of the experimental molecular shape with that of pyridine shows that negligible molecular deformations occur when fusing two six-membered rings.

N.M.R. spectroscopy of molecules partially oriented in liquid crystalline solvents has been recognized as a very reliable method for determining molecular structures.<sup>1,2</sup> Owing to the known physical limitation only ratios of interprotonic distances can be obtained and therefore bond angles rather than bond lengths can be defined.<sup>3,2</sup>

A number of studies on molecules formed by two fused aromatic six-membered rings have been recently carried out in this way: the structure of naphthalene<sup>3</sup> has been compared with that obtained from neutron diffraction and two diazanaphthalenes<sup>4,5</sup> (whose structures have not been previously determined) investigated.

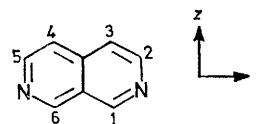
Naphthyridines contain one nitrogen atom in each of the two six-membered rings and may be thus considered as formed by two pyridine molecules. It is therefore interesting to see if any modifications occur in the pyridine ring when two of them are fused together into a

<sup>1</sup> P. Diehl and C. L. Khetrapal in 'N.M.R. Basic Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer Verlag, New York, 1969, vol. 1, p. 1.

<sup>2</sup> L. Lunazzi in 'Determination of Organic Structures by Physical Methods,' eds. F. C. Nachod, J. J. Zuckermann, and E. W. Randall, Academic Press, New York, vol.6.

<sup>3</sup> J. M. Dereppe, E. Arte, and M. Van Meerssche, *J. Mol. Structure*, 1973, **17**, 225.

single molecule. An analogous study has been already reported for two fused thiophen rings<sup>6</sup> and an investigation on 4,4'-bipyridyl did show that hydrogens in positions 3 and 5 are bent toward the nitrogen atom owing to the steric hindrance of the second ring.<sup>7</sup>



The 100 MHz spectrum of the 2,7-naphthyridine partially oriented in a nematic phase has been obtained (Figure) and interpreted in terms of dipolar couplings, chemical shifts, and assumed  $J_{HH}$  values. The figures reported in Table I have been used for simulating the theoretical spectrum.

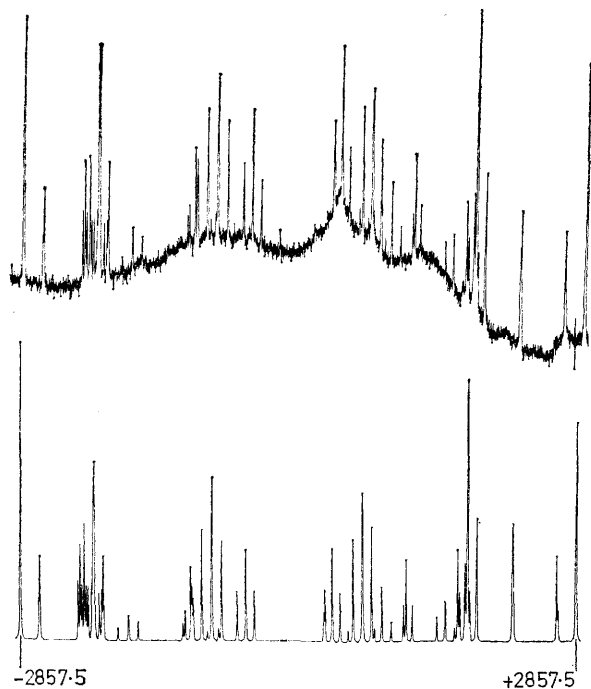
<sup>4</sup> C. L. Khetrapal and A. C. Kunwar, *Mol. Cryst. Liquid Crystals*, 1972, **15**, 363.

<sup>5</sup> C. L. Khetrapal, A. Saupe, and A. C. Kunwar, *Mol. Cryst. Liquid Crystals*, 1972, **17**, 121.

<sup>6</sup> C. A. Boicelli, A. Mangini, L. Lunazzi, and M. Tiecco, *J.C.S. Perkin II*, 1972, 192.

<sup>7</sup> J. W. Emsley, D. S. Stephenson, J. C. Lindon, L. Lunazzi, and S. Pulga, *J.C.S. Perkin II*, 1975, 1541.

It has been observed that an exchange of the dipolar couplings  $D_{12}$  and  $D_{15}$  only affects the intensities of two out of the 60 lines of the spectrum, thus leaving some



Experimental (top) and computed 100 MHz n.m.r. spectrum of 2,7-naphthyridine partially oriented in the nematic phase (Licrystal Phase IV) at the probe temperature. The computed spectrum has been obtained using a line width of 6.0 Hz

TABLE 1

Dipolar couplings and chemical shifts (Hz) of the 100 MHz n.m.r. spectrum of 2,7-naphthyridine dissolved in nematic phase. The chemical shifts are referred to the centre of the spectrum; the  $J_{HH}$  values, taken from the isotropic spectrum, are 6.0 Hz ( $J_{23}$ ) and 0.8 Hz ( $J_{13}$  and  $J_{14}$ )

	$\nu_1 - 186.3$	$\nu_2 - 132.8$	$\nu_3 + 9.6$
$D_{12}$	-102.7		$D_{16}$ -2 552.6
$D_{13}$	+49.5		$D_{23}$ -1 741.6
$D_{14}$	-27.6		$D_{24}$ -319.2
$D_{15}$	-124.8		$D_{25}$ -134.0
			$D_{34}$ -2 238.2

uncertainty on the interpretation. Such an inversion however would lead to a set of data internally inconsistent with the molecular geometry and can be safely dismissed.

<sup>8</sup> B. Bæk, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1958, **2**, 361; G. O. Sorensen, L. Mahler, and N. Rastrup-Andersen, *J. Mol. Structure*, 1974, **20**, 119.

From experimental dipolar couplings interprotonic distances and orientational parameters can be obtained if an interprotonic distance is assumed [equation (1)].<sup>1,2</sup>

$$D_{ij} = \frac{\hbar}{2\pi} \gamma_i \gamma_j \left\langle \frac{3\cos^2\theta_{ij} - 1}{r_{ij}^3} \right\rangle \quad (1)$$

In the present case the distance H(2)-H(3) was taken equal to that of pyridine as determined by microwave measurements (2.483<sub>3</sub> Å).<sup>8</sup>

The distance ratios obtained in this way are reported in Table 2 in which are also listed the ratios calculated

TABLE 2

Ratios of interprotonic distances and orientational parameters of 2,7-naphthyridine as obtained from liquid crystal n.m.r. The ratios obtained by 'building up' the same molecule using the geometry of pyridine<sup>8</sup> are also reported. The  $S_{ij}$  values are based on a H(2)-H(3) distance of 2.483<sub>3</sub> Å

$r_{ij}/r_{23}$	Experimental	Computed	Deviation (%)
12	1.641 ± 0.006	1.656	0.85
13	1.963 ± 0.010	1.967	0.20
14	2.223 ± 0.010	2.217	0.27
15	2.339 ± 0.005	2.341	0.08
16	1.020 ± 0.003	1.012	0.78
23	1.000		
24	1.975 ± 0.003	1.949	1.31
25	2.723 ± 0.009	2.710	0.47
34	1.065 ± 0.004	1.033	3.00
$S_{xx} = 0.1726 \pm 0.0018$		$S_{zz} = -0.0239 \pm 0.0006$	

assuming a structure formed by two fused pyridine rings sharing the appropriate carbon-carbon bond. The average deviation is only 0.87%, the largest being 3.0%; it seems therefore that no appreciable modification is expected to occur when two six-membered rings are fused. The small deviations can be, in part, due to the neglect of the vibrational corrections.<sup>7</sup>

## EXPERIMENTAL

2,7-Naphthyridine was synthesised according to ref. 9. The nematogen used for orienting the molecule was Merck Licrystal Phase IV<sup>2</sup> which can orient a convenient amount of solute at the probe temperature. The theoretical interpretation was carried out by means of the iterative program LAOCNOR using all 60 resolved spectral lines; in the refining of the molecular structure the program SHAPE was used (courtesy of Professor P. Diehl, University of Basel).

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<sup>9</sup> P. Cavalieri D'Oro, R. Danieli, G. Maccagnani, G. F. Pedulli, and P. Palmieri, *Mol. Phys.*, 1971, **2**, 365.