Structure and Conformation of 4,4′-Bipyridyl by Nuclear Magnetic Resonance Spectroscopy of a Nematic Solution

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The 200 MHz ^{1}H n.m.r. spectrum of 4,4′-bipyridyl dissolved in the nematic liquid crystal, Phase V, has been obtained and analysed. The dipolar couplings are shown to be consistent with rapid rotation about the inter-ring C–C bond, such that only four positions are appreciably populated, each having an inter-ring angle of 29.6 ± 0.01°. This implies that the barrier to rotation $V(\theta)$ of the molecule dissolved in the liquid crystal has maxima at 0 (planar) and 90° which are both relatively high, and that $V(90°)$ is greater than $V(0°)$. These conclusions are obtained only if vibrational averaging of the dipolar couplings is carried out.

THE study of molecular structure by recording and analysing the n.m.r. spectrum of a partially oriented liquid sample is now established as complementary to the well known techniques of *X*-ray and electron diffraction, and microwave spectroscopy.[1] Possibly the most interesting aspect of the n.m.r. method is the information which can be obtained about internal motion in a

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[1] L. Lunazzi, ' Determination of Organic Structures by Physical Methods,' eds. J. J. Zuckerman and E. W. Randall, Academic Press, New York, 1975, vol. 6.

molecule. There are, however, difficulties in the interpretation of the experimental data, the consequences of which have yet to be fully explored. The principal difficulty is how to average dipolar coupling constants, D_{ij}, over all internal motions. A molecule like 4,4′-bipyridyl exhibits two kinds of internal motion, the large amplitude rotation about the inter-ring C–C bond, and small amplitude vibrational motion. At room temperature both kinds of motion are faster than $(D_{ij})^{-1}$, hence only averaged D_{ij} values are observed. It has been usual to assume that these two kinds of motion can be treated separately, thus neglecting any possible interdependence, and furthermore, it has been the practice to assume that the effect of small amplitude vibrations can be neglected.

The large amplitude motion is characterised by the potential energy $V(\theta)$. The angular dependence of $V(\theta)$ is constrained to have reflection symmetry about $\theta = 0$, $\pi/2$, and π and thus expanding $V(\theta)$ as a Fourier series gives equation (1). $V(\theta)$ should be substituted

$$V(\theta) = V_2\,(1 - \cos 2\theta)/2 + V_4\,(1 + \cos 4\theta)/2 + V_8\,(1 + \cos 8\theta)/2 + \ldots \quad (1)$$

into the Schrodinger equation for rotation and solved for the rotational wavefunction.[2] However, it is a good approximation to assume that rotational probabilities p(θ) are given by (2) and an averaged dipolar coupling

$$p(\theta) = \exp\,[-V(\theta)]\Big/\int_0^{2\pi} \exp\,[-V(\theta)]\mathrm{d}\theta \quad (2)$$

constant is given by (3).

$$\langle D_{ij}\rangle = \int_0^{2\pi} p(\theta)\, D_{ij}(\theta)\,\mathrm{d}\theta \quad (3)$$

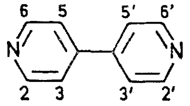
In a study of *p,p′*-dichlorobiphenyl Diehl *et al.*[3] considered first a model in which the molecule exists only at the minimum in $V(\theta)$, a situation consistent with both V_2 and V_4 large and V_8 small. This model was rejected because the difference, $\Delta D_{22'}$, between the observed and calculated dipolar coupling between protons at positions 2 and 2′ (using the same labelling as for bipyridyl, shown in Table 1) was found to be 1.1%, an unacceptable value compared with the experimental errors. Diehl *et al.*[3] argued that the large value of $\Delta D_{22'}$ shows that the inter-ring dipolar couplings are sensitive to the form of $V(\theta)$. We present here a study of the similar molecule, 4,4′-bipyridyl, in order to see if here also the dipolar couplings are sensitive to $V(\theta)$. We also examine the effect of averaging dipolar coupling over vibrational motion.

EXPERIMENTAL

The sample of 4,4′-bipyridyl was a commercial product and used without further purification. The nematogen was Merck Phase V and having a nematic range from −5 to 75°. The concentration of the solute was that of a saturated solution at 20° Spectra were obtained on a Varian HR 220 spectrometer, and have a total width of >19 kHz. The spectrum was recorded in four overlapping 5 000 Hz segments. The average linewidth is 15 Hz, and line positions were measured to a precision of 5 Hz.

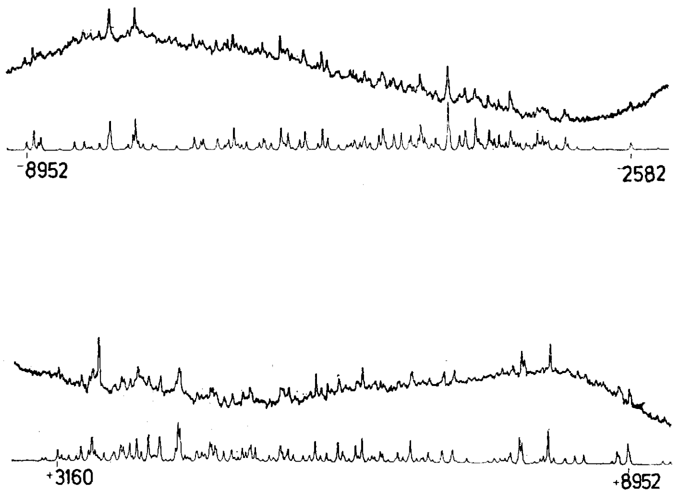
TABLE 1

N.m.r. parameters for 4,4′-bipyridyl dissolved in the nematic phase of Merck Phase V



Dipolar coupling (D_{ij}/Hz)	
2,3	−3 532.1 ± 0.2
3,6	30.9 ± 0.2
3,5	286.0 ± 0.4
3,3′	−1 458.9 ± 0.3
3,2′	−302.2 ± 0.2
2,6	328.8 ± 0.4
2,2′	−112.2 ± 0.3
Chemical shifts [ν_i (p.p.m.)]	
3	0
2	0.571 ± 0.004
Isotropic coupling constants (J_{ij}/Hz) [5]	
2,3	5.5
2,5	0.9
3,5	1.6
2,6	0.4

Spectral Analysis.—The spectra were analysed as an AA′A″A‴BB′B″B‴ spin system using the program LAOCOONOR.[4] A total of 152 lines were used in the fitting process and a final r.m.s. error of 4.7 Hz was obtained. The Figure shows observed and calculated spectra, and in Table 1 are the values of dipolar couplings and chemical shifts. The isotropic spin coupling constants, J_{ij}, were kept



220 MHz ^{1}H n.m.r. spectrum of 4,4′-bipyridyl dissolved in the nematogen Phase IV. The spectrum is displayed with the central part omitted since there are no observed lines in this region. The upper trace is the observed and the lower the calculated spectrum

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[2] P. Bucci, M. Longeri, C. A. Veracini, and L. Lunazzi, *J. Amer. Chem. Soc.*, 1974, **96**, 1305.

[3] P. Diehl, W. Niederberger, and L. Lunazzi, *Mol. Phys.*, 1973, **26**, 571.

[4] P. Diehl, C. L. Khetrepal, and H. P. Kellerhals, *Mol. Phys.*, 1968, **15**, 333.

fixed in the analysis at the values determined for pyridine[5] for an isotropic solution.

RESULTS AND DISCUSSION

The dipolar coupling between two nuclei is related to the relative nuclear positions *via* relationship (4) where

$$
\begin{aligned}
D_{ij} = &-\frac{\gamma_i\gamma_j h}{8\pi^2 r_{ij}^3}\,[S_{zz}(3\cos^2\theta_{ijz} - 1) + (S_{xx} - S_{yy})(\cos^2\theta_{ijx} - \cos^2\theta_{ijy}) + 2S_{xy}\cos\theta_{ijx}\cos\theta_{ijy} + 2S_{xz}\cos\theta_{ijx}\cos\theta_{ijk} + 2S_{yz}\cos\theta_{ijy}\cos\theta_{ijz}] \\
&-\frac{\gamma_i\gamma_j h}{8\pi^2}\,[S_{zz}(2f\tau_{ijzz} - f_{ijxx} - f_{ijyy}) + (S_{xx} - S_{yy})(f_{ijxx} - f_{ijyy}) + 2S_{xy}f_{ijxy} + 2S_{xz}f_{ijxz} + 2S_{yz}f_{ijxz}] \qquad (4)
\end{aligned}
$$

the $S_{\alpha\beta}$ are elements of the ordering matrix, and the $f_{ij\alpha\beta}$ are correction terms for harmonic vibrational motion. Equations for the $f_{ij\alpha\beta}$ have been given by Lucas.[6] If the z-axis is chosen to be the long axis of the molecule as shown in Table 1, then the terms involving off-diagonal elements of $S_{\alpha\beta}$ in equation (4) vanish. This arises because internal rotation creates two effective mirror planes xz and yz.[7] It should be noted that the diagonalisation of $S_{\alpha\beta}$ in the xyz axis system arises when the rate of internal rotation is greater than the quantity $(D_{ij})^{-1}$ and does not depend upon the relative rates of internal rotation, ν_{int}, and whole-molecule reorientation ν_{mol}. When $\nu_{\text{int}} \gg \nu_{\text{mol}}$ then a single set of averaged $S_{\alpha\alpha}$ elements can be used in equation (1), but if this condition is not met there will be distinct values of $S_{\alpha\alpha}$ for each value of θ. Clearly the latter case is intractable (and must be assumed not true).

TABLE 2

Inter-nuclear distances (Å) and molecular orientation parameter $S_{\alpha\beta}$ for 4,4′-bipyridyl derived (a) with and (b) without vibrational averaging

	(a)	(b)	Pyridine (n.m.r.)[8]	Pyridine (microwave)[a]
r_{23}	2.451 ± 0.0001	2.459 ± 0.007	2.482 ± 0.02	2.483
r_{25}	4.866 ± 0.0001	4.869 ± 0.008	4.866 ± 0.04	4.886
r_{35}	4.306 ± 0.0001	4.302 ± 0.003	4.269 ± 0.02	4.306
r_{26} *	4.105	4.105	4.105	4.112
$r_{33'}$	2.258 ± 0.0001	2.233 ± 0.007		
$z_{3'} - z_3$	1.993 ± 0.0001	1.926 ± 0.003		
θ	29.58 ± 0.001	29.35 ± 0.03		
S_{zz}	0.453 ± 0.0001	0.438 ± 0.001		
$S_{xx} - S_{yy}$	0.0667 ± 0.0006	0.0592 ± 0.0006		
R.m.s. error	0.01 Hz	0.7 Hz		

* Fixed.

[a] B. Bak, L. Hansen-Nygarre, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1958, **2**, 361.

We have first considered the model of 4,4′-bipyridyl which assumes that a single angle θ between the planes of the two pyridine rings is sufficient to describe the structure. The molecule is assumed to spend equal amounts of time in the positions related by the xz and yz mirror planes. In order to calculate the correction terms $f_{ij\alpha\alpha}$ in equation (4) it is necessary to carry out a normal co-ordinate analysis for the molecule. We have calculated the frequencies, ν_k, and the $L_{ik\alpha}$ matrix[6] by taking the force field determined for pyridine[8] and for the extra internal co-ordinates we have used values given by Eaton and Steele[9] for biphenyl.

This model of 4,4′-bipyridyl is completely described for our purposes by four relative inter-proton co-ordinates, including the inter-ring angle θ as one co-ordinate; thus, as two $S_{\alpha\alpha}$ elements are also necessary to calculate the D_{ij} values there are six unknown parameters to determine from seven experimental dipolar couplings. To determine the parameters we use a least-squares method, and the results are given in Table 2. The distance r_{35} was chosen as the reference length, and given the value found by n.m.r. studies on [^{15}N]pyridine in a nematic phase.[8,10] The inter-nuclear distances are given in Table 2 together with the values found for pyridine in order to compare structural changes in the two compounds. The ring geometries of the two compounds are very similar; in 4,4′-bipyridyl there is a small increase in r_{35} and a decrease in r_{23} compared with pyridine, reflecting the steric influence of the other ring. Note that vibrational averaging has a large effect (3%) on the inter-ring separation, as measured by the difference $z_{3'} - z_3$. If the carbon framework in each ring of bipyridyl is assumed unchanged from that in pyridine, and if the angle C(3) C(2) H(2) and the C(2)–H(2) bond length are also unchanged, then the inter-ring C–C bond length in bipyridyl is found to be 1.500 Å. An electron diffraction study[11] on a gaseous sample found a C–C inter-ring distance of 1.470 Å, and an inter-ring angle of 37.2°.

The results without vibrational averaging for 4,4′-bipyridyl exactly parallel those for the 4,4′-dichlorobiphenyl in that $\Delta D_{22'}$ is found to be 1.6% in the former, and 1.1% in the latter compound. But the effect of vibrational averaging on the bipyridyl results is to make all residual ΔD_{ij} values small, and to considerably improve the total r.m.s. error between observed and

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[5] S. Castellano, C. Sun, and R. Kostelnik, *J. Chem. Phys.*, 1967, **46**, 327.

[6] N. J. D. Lucas, *Mol. Phys.*, 1971, **22**, 233.

[7] A. Saupe, *Z. Naturforsch.*, 1965, **20a**, 572.

[8] J. W. Emsley, J. C. Lindon, and J. Tabony, *J.C.S. Faraday II*, 1975, **71**, 579.

[9] V. Eaton and D. Steele, *J.C.S. Faraday II*, 1973, 1601.

[10] C. Schumann and R. Price, *Angew. Chem.*, 1973, **85**, 989.

[11] A. Almeningen and O. Bastiansen, *Kgl. Norske Vindeslab. Selkabs. Skrifter*, 1958, 1 (*Chem. Abs.*, 1959, **53**, 11,917c).

calculated dipolar couplings; $\Delta D_{22'}$ at 0.02% is the largest residual. We conclude that for 4,4′-bipyridyl the model of a deep potential well at 29.58° between planar and perpendicular structures is in complete accord with the dipolar couplings. The vibrational amplitudes for protons in 4,4′-dichlorobiphenyl must be very similar to those in 4,4′-bipyridyl and we can confidently conclude that the large value of $\Delta D_{22'}$ found by Diehl *et al.*[3] is a result of neglecting vibrational averaging.

It would seem at first sight that the success of calculations with a fixed θ means that no information can be deduced about V_2 and V_4. However, if V_8 is assumed zero, which is consistent with the shapes of $V(\theta)$ calculated for biphenyl compounds by molecular orbital methods,[12–15] then the minimum in the function is obtained by differentiating equation (1) to give (5) which

$$\theta(\text{minimum}) = \cos^{-1}[0.5 + V_2/8V_4]^{\frac{1}{2}} \qquad (5)$$

for $\theta = 29.58°$ gives $V_2/V_4 = 2.06$. Also, since we find that the inter-ring dipolar couplings are accounted for by assuming the molecule spends all its time with θ near the minimum value, then the values of $V(0°)$ and $V(90°)$ must be greater than *ca.* 12 kJ mol^{-1}. The important result is that $V(0°)$ must be less than $V(90°)$, which is true when θ(minimum) is less than 45°. This conflicts with most of the theoretical calculations on 4,4′-bipyridyl[13] and on biphenyl[12,14] which find $V(0°) > V(90°)$, and only one calculation on biphenyl has found the reverse.[15]

However, it should be remembered that the n.m.r. data refer to a liquid crystal phase whilst calculations are relevant to isolated molecules. There may be intermolecular contributions to V_2 and V_4 which influence θ(minimum) in a manner similar to those which make θ(minimum) = 0° in the solid state of biphenyl.[16,17]

It is interesting to compare our results with those found by neglecting vibrational averaging and reducing $\Delta D_{22'}$ by averaging the inter-ring dipolar couplings $D_{22'}$, $D_{23'}$, and $D_{33'}$ over the internal motion. Assuming V_8 in equation (1) to be zero and varying V_2, V_4 and the inter-ring separation to give exact agreement between calculated and observed dipolar couplings, gives $V_2 = 14.6$ and $V_4 = 10.7$ kJ mol^{-1}, and θ(minimum) = 36°. The two approaches to the problem therefore do not disagree on the general conclusion that $V(0°)$ is less than $V(90°)$ (10.7 against 19.9 kJ mol^{-1} respectively).

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[12] G. Casalone, C. Mariani, A. Mugnoli, and M. Simonetta, *Mol. Phys.*, 1968, **15**, 339.

[13] V. Galasso, G. De Alti, and A. Bigotto, *Tetrahedron*, 1971, **27**, 991.

[14] M. J. S. Dewar and A. J. Harget, *Proc. Roy. Soc.*, 1970, **A315**, 443.

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[16] J. Trotter, *Acta Cryst.*, 1961, **14**, 1135.

[17] A. Hargreaves and S. Hasan-Rizvi, *Acta Cryst.*, 1962, **15**, 365.