Nematic-phase Nuclear Magnetic Resonance Investigation of Rotational Isomerism. Part 7.† An Investigation into the Structure of 2,2′-Bipyridyl using the Proton and Deuterium Spectra of Liquid Crystalline Solutions

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A 220 MHz proton n.m.r. spectrum of 2,2′-bipyridyl in a nematic phase solution has been analysed to yield a set of dipolar coupling constants, D_{ij}. The couplings D_{ij} are not in complete agreement with a description of the molecule as a single conformation. The *trans*-form alone occurs in solid, 2,2′-bipyridyl, but although this is probably the predominant form in the liquid state, there does appear to be a difference between the molecular structure in the two phases.

X-RAY[1] and electron diffraction[2] studies of 2,2′-bipyridyl determined that the molecule was planar and had an N,N *trans*-conformation. An e.s.r. study on the radical anion in solution, however, has been interpreted as showing the molecule to have an N,N *cis*-structure, which may be caused by complex formation with the counter-ion.[3,4] Biphenyls are well-known examples of molecules whose structure can change in going from the solid to the liquid phase, and the structure in the liquid phase may be determined, in principle, from the set of partially-averaged, dipolar coupling constants, D_{ij}, determined from the analysis of proton n.m.r. spectra of liquid crystalline solutions.[5,6] Thus, the molecules 4,4′-dichlorobiphenyl[7] and 4,4′-bipyridyl[8] have been shown to be non-planar in solution, in contrast to their planar structures in the crystalline state. We now report a study of 2,2′-bipyridyl using both proton and deuterium spectra of nematic solutions. Deuterium spectroscopy has the advantage that the spectra, even of eight-spin systems as in 2,2′-[$^2H_8$]bipyridyl, are simple to interpret. If a structure is assumed the spectra yield values of ordering matrix elements, which may be used to calculate trial parameters for the analysis of the much more complex proton spectra.

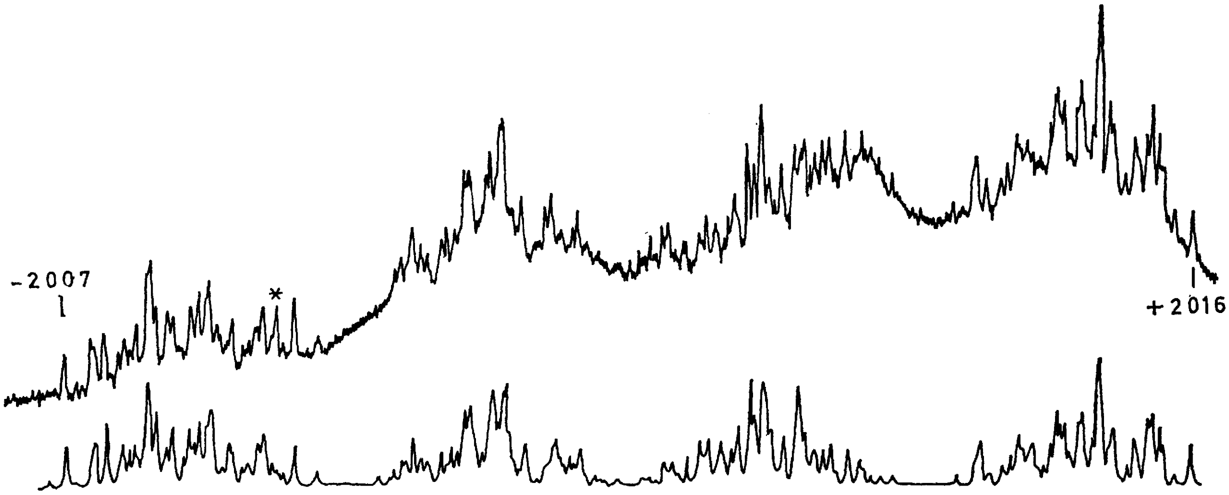

FIGURE 1 The proton n.m.r. spectrum at 220 MHz of 2,2′-bipyridyl dissolved in the nematogen phase IV

EXPERIMENTAL

The sample of 2,2′-bipyridyl was obtained from Koch–Light, and the nematogen was Merck Phase IV. The proton spectrum was recorded on a Varian HR 220 MHz spectrometer, and is shown in Figure 1.

Three samples of 2,2′-[$^2H_8$]bipyridyl were prepared and used in the n.m.r. experiments. A sample was prepared by synthesis from deuteriated starting materials: pentadeuteriopyridine with sodium amide ($NaNH_2$) in anhydrous toluene at 110 °C gave 2-aminopyridine deuteriated in positions 3, 4, 5, and 6. Treatment of the 2-aminopyridine with $NaNO_2$ and bromine yields 2-bromopyridine with retention of the deuterium atoms. The 2,2′-[$^2H_8$]bipyridyl was obtained by reaction of the 2-bromopyridine with copper. Two samples of 2,2′-[$^2H_8$]bipyridyl were synthesized by a procedure developed previously[9] for the deuteriation of pyridine using heterogeneous metal-catalysed exchange with D_2O. A sample of 2,2′-bipyridyl

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† Part 6, L. Lunazzi, P. Bellamo, C. A. Veracini, and A. Amanzi, *J.C.S. Perkin II*, 1979, 559.

was exchanged with D_2O at 130 °C for three days in the presence of platinum prepared by borohydride reduction of platinum oxide.[9] Platinum was chosen as catalyst because it is known to promote exchange in all protons of pyridine. Reagent quantities were chosen to give 80% deuteriation at equilibrium in one pass. The extent of total deuteriation may be varied by repeated exchange cycles, thus a single cycle gave 34% and two cycles 76 atom % ^{2}H. The site distribution of ^{2}H changes with each cycle, and hence it is possible to assign resonance peaks from relative intensities. The 34% ^{2}H sample gave a ^{2}H spectrum, when dissolved in a liquid crystal, which had one peak almost double the intensity of the other three and which was assigned to the ^{2}H in positions 6,6′ on the basis of the susceptibility of these positions to ^{2}H replacement.

The deuterium spectra were recorded on a Varian XL100 spectrometer, operating in the pulse Fourier transform mode. The spin-lattice relaxation times of the ^{2}H nuclei were determined to be < 50 ms and hence spectra could be recorded with an acquisition time for the free induction decays of 0.1 s, giving a resolution of 10 Hz. Figure 2 shows a ^{2}H spectrum of 2,2′-[$^2H_8$]bipyridyl in the nematogen 4-ethoxybenzylidene-4-n-butylaniline (EBBA), obtained from Eastman Organic Chemicals.

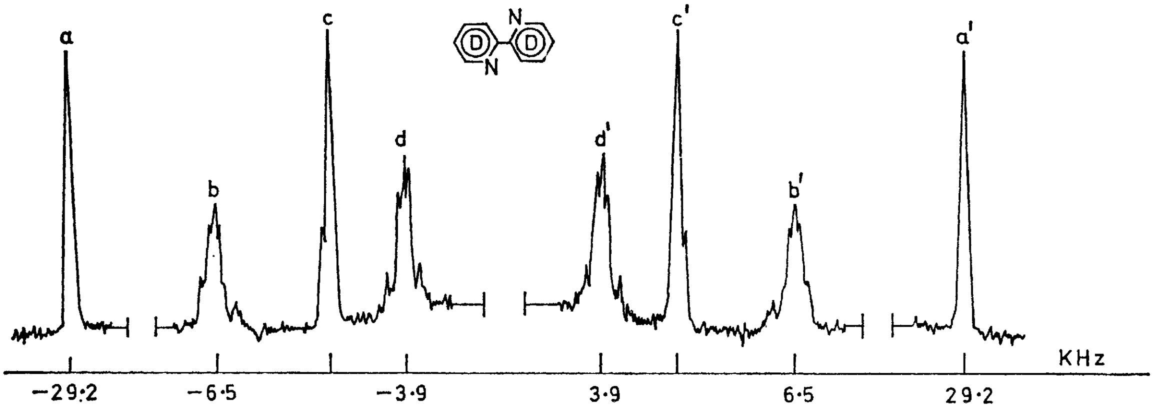
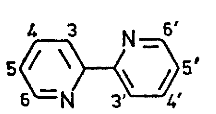


FIGURE 2 The deuterium n.m.r. spectrum at 15.35 MHz of 2,2′-[$^2H_8$]bipyridyl dissolved in the nematogen EBBA

TABLE 1

N.m.r. parameters obtained from the analysis of the 220 MHz proton spectrum of 2,2′-bipyridyl dissolved in the nematic phase of Merck Phase IV



i,j	D_{ij} (Hz)	J_{ij} (Hz) *	δ_{ij} (p.p.m.)
3,4	$-1\,016.9 \pm 0.3$	8.01	0.70 ± 0.01
3,5	-133.0 ± 0.4	1.16	0.87 ± 0.01
3,6	-25.3 ± 0.4	1.0	-0.31 ± 0.01
3,3′	-29.6 ± 0.6	0.0	
3,4′	-39.1 ± 0.3	0.0	
3,5′	-63.1 ± 0.4	0.0	
3,6′	-222.5 ± 0.5	0.0	
4,5	-154.3 ± 0.5	7.53	0.17 ± 0.01
4,6	11.2 ± 0.5	1.8	-1.0 ± 0.01
4,4′	-21.1 ± 0.6	0.0	
4,5′	-30.6 ± 0.6	0.0	
4,6′	-67.3 ± 0.3	0.0	
5,5′	-27.1 ± 0.6	0.0	
5,6′	-29.1 ± 0.4	0.0	
6,6′	-23.8 ± 0.4	0.0	

* Set constant at values found for pyridine.

Analysis of Spectra.—The proton spectrum was analysed with the aid of the computer program LAOCN 3, modified for dipolar couplings, and altered to calculate the spectrum of eight protons. The analysis of the proton spectrum in isolation proved a difficult task, because of the uncertainty about the structure and that the probable structure, the N,N *trans*-form, has C_{2h} symmetry, and hence the relationship between dipolar couplings and structure requires three $S_{\alpha\beta}$ values for any axis system with x and y in the molecular plane. Our successful approach was to use the deuterium spectra to obtain good estimates of $S_{\alpha\beta}$, assuming a N,N *trans*-structure. The deuterium spectrum should be recorded under the same conditions as the proton, but this did not prove to be practicable. The proton spectrum was recorded on a Varian 220 MHz spectrometer, and was much better resolved than spectra obtained at 100 MHz on a Varian XL100. Attempts to analyse proton spectra obtained at 100 MHz have so far proved unsuccessful. The deuterium splittings, Δν, for the spectrum shown in Figure 2 are given in Table 2 and interpreted as follows: the peaks marked a,a′ and having the largest splitting, Δν, were assigned to deuteriums in positions 5 and 5′. Molecules like 2,2′-bipyridyl are most probably oriented with their long axis tending to lie parallel to the field direction, and hence the order parameter S_{CD} for the bonds C(5)–D(5) and C(5)–D(5′) is expected to be the largest of the four C–D bond-order parameters. The values of Δν and S_{CD} are related by

$$\Delta\nu = \tfrac{3}{2} S_{CD} q_{CD} \qquad (1)$$

where q_{CD} is the deuterium quadrupole coupling constant for the C–D bond,[6] and equation (1) assumes that the electric field gradient tensor for C–D bonds is cylindrically symmetric. The value of q_{CD} does not vary by more than

TABLE 2

Peak separations, Δν, in the deuterium spectrum of 2,2′-[$^2H_8$]bipyridyl dissolved in the nematic phase of EBBA

Nucleus	Δν/Hz
3	$7\,740 \pm 50$
4	$13\,060 \pm 50$
5	$58\,400 \pm 50$
6	$9\,830 \pm 50$

± 5 kHz for aromatic CD bonds, and has an average value [6] of 185 kHz. Using this numerical value in equation (1) enables S_{CD} to be calculated for the C(5)–D(5) bond and to be equated, approximately, to S_{xx}. The assignment of peaks (c,c′), (b,b′), and (d,d′) is more conjectural. Peaks (c,c′) most probably arise from the deuterium atoms in positions 6 and 6′. We make this assignment on the basis of intensity, discussed above, and because it is the narrowest peak, the deuteriums in these positions being expected to have smaller couplings to neighbouring deuteriums than either of the deuteriums in positions 3 or 4. The other two pairs of peaks are much broader because of the larger coupling between deuteriums in positions 3 and 4, and can not be assigned with certainty. We resort, therefore, to assuming first that C–D bonds to deuteriums in positions 3, 4, and 6 make an angle of 60° to the x-axis, and assuming that S_{xy} is zero, we obtain a value for S_{yy} by taking the mean value of the splittings $\Delta\nu_3$, $\Delta\nu_4$, and $\Delta\nu_6$. This procedure gives S_{xx} and $(S_{yy} - S_{zz})$ and we then calculate a set of inter-proton dipolar couplings with these values using the structure determined by X-rays. The dipolar couplings were used to calculate a proton spectrum, which had considerable similarity to that observed, and it was possible to obtain line assignments and to proceed to iterative calculations. Table 1 gives the results of analysing the 220 MHz proton spectrum, and it should be noted that the couplings $D_{64'}$ and $D_{53'}$ may be interchanged, as may $D_{66'}$ and $D_{44'}$, without an appreciable change in the spectrum. We have, therefore, used the sum of these pairs in the structure determination.

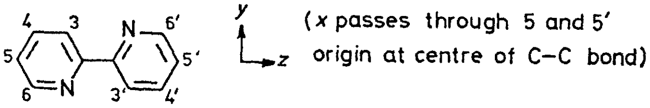
Vibrational Corrections.—Precise structure determinations must allow for the averaging of dipolar couplings over vibrational motion. A procedure for correcting for harmonic motion has been proposed by Lucas,[10] which requires a knowledge of the matrix $L_{ik\alpha}$ connecting Cartesian displacements with normal co-ordinates. There has not been a vibrational analysis of this molecule and, consequently, we have adopted a purely theoretical approach. We have used a force field based on that derived for biphenyl and used for 4,4′-bipyridyl.[7] The effect of vibrational averaging is small, and errors in our force field will not affect the conclusions reached on the structure of the molecule. Details of the force field are not given here, but may be obtained on request.

RESULTS AND DISCUSSION

Since all conformations of 2,2′-bipyridyl possess a C_2 axis of symmetry, which we choose as z, to relate dipolar couplings to a single structure requires the three elements S_{zz}, $S_{xx} - S_{yy}$, and S_{xy} of the Saupe ordering matrix. By fixing x to pass through protons 5 and 5′ we reduce the unknown proton co-ordinates to a minimum set of seven, which is further reduced to six independent co-ordinates when we make the necessary assumption of one fixed interproton distance, provided that the molecule is assumed to have planar pyridine rings and a known inter-ring angle. Thus, there are 9 unknown structural parameters for a given inter-ring angle compared with 16 dipolar couplings (which is reduced to 14 by allowing for the deceptive simplicity discussed earlier).

TABLE 3

Co-ordinates in angstroms, order parameter, $S_{\alpha\beta}$, and ΔD_{ij}, dipolar coupling constant residuals (Hz) derived assuming a planar *trans*-form of 2,2′-bipyridyl



x_6	3.19 ± 0.09	r_{56}	2.48	(2.48) *
x_6	-2.09 ± 0.03	r_{46}	4.39 ± 0.24	(4.30)
x_5	4.52 ± 0.09	r_{36}	4.70 ± 0.23	(4.89)
x_4	3.01 ± 0.07	r_{45}	2.74 ± 0.21	(2.51)
y_4	2.29 ± 0.05	r_{46}	4.24 ± 0.20	(4.27)
x_3	0.74 ± 0.03	r_{34}	2.30 ± 0.23	(2.51)
y_3	1.92 ± 0.08			
S_{xx}	0.115 ± 0.007			
S_{yy}	-0.007 ± 0.007			
S_{yy}	0.016 ± 0.002			

$\Delta D_{5.6}$†	-0.2	$\Delta D_{5.6'}$	5.0	$\Delta D_{3.5}$	-1.2	$\Delta D_{3,4'}$	0.9
$\Delta D_{4.6}$	-0.5	$(\Delta D_{4.6'} + \Delta D_{3.5'})$	0.3	$\Delta D_{5.5'}$	8.4	$\Delta D_{3.3'}$	1.2
$\Delta D_{3.6}$	1.6	$\Delta D_{3,6'}$	-0.6	$\Delta_{4.5'}$	3.7		
$(\Delta D_{6.6'} + \Delta D_{3,3'})$	3.8	$\Delta D_{4.5}$	-0.2	ΔD_{34}	-0.1		

* $r_{5.6}$ Fixed. The values in parentheses are the distances found for pyridine by microwave spectroscopy. † $\Delta D_{ij} = D_{ij}$ (calc.) $- D_{ij}$ (obs.).

We have tested the hypothesis that the molecule is a single conformation, that is the variation of the potential energy, $V(\theta)$, with the inter-ring angle, θ, has a single, deep minimum. It was found that θ must be close to zero corresponding to the *trans*-form in order to have a minimum in the RMS error, R, between observed and calculated dipolar couplings. In Table 3 we give the co-ordinates and order parameters calculated for the planar *trans*-form, and also the residuals, ΔD_{ij}, between calculated and observed dipolar couplings. The minimum in R occurs at $\theta = 15°$, but the difference between R for $\theta = 0°$ and 15° is small and the ΔD_{ij} values over this range of θ are very similar; we give, therefore, the data only for the *trans*-structure. Although the ΔD_{ij} values are at a minimum for structures close to $\theta = 0°$, there are some unacceptably large individual ΔD_{ij} values, and hence the model must be rejected as giving an incomplete account of the observed dipolar couplings. The data in Table 3 are based on fixing $r_{56} = 2.48$ Å, a value appropriate for pyridine, and the distribution of residuals is dependent on this choice. Fixing some other inter-proton distance changes the distribution of residuals, but for all choices there always remain some large individual values.

We conclude, therefore, that the *trans*-structure, although giving predicted dipolar couplings close to those observed, does not give an acceptable fit to all the data, and hence the liquid state structure probably differs from that in the crystalline solid. This conclusion is supported by the CNDO/2 molecular orbital calculations of Bergen *et al.*,[11] who find that $V(\theta)$ is almost constant between $\theta = \pm 70°$, with a minimum near $\pm 30°$ which is only 500 J mol^{-1} lower than $C(0°)$.

We have tried fitting the observed dipolar couplings by averaging over internal rotation about the x-axis, such that each value of θ is weighted by $P(\theta) = [e^{-V(\theta)/RT}][\sum_{\theta} e^{-V(\ )/RT}]^{-1}$. To do this it is necessary to assume that the relative co-ordinates within each ring are independent of θ, as also is the inter-ring separation. We must also assume that rotation about x is more rapid than the rate of reorientation of the whole molecule in the liquid crystal, so that all conformations are described by a single, averaged $\boldsymbol{S}$ matrix. With these restrictions the dipolar couplings within each ring are related to the average $\boldsymbol{S}$ matrix and the nuclear positions independently of the value of θ, as also is the value of the inter-ring coupling $D_{55'}$. Unfortunately there are seven such dipolar couplings, but nine structural unknowns. To make $D_{55'}$ independent of θ it is necessary to fix $r_{55'}$ and S_{xx}, which leaves six dipolar couplings, but 8 unknowns. Fixing x_6 and y_6 at values appropriate to the X-ray structure gives co-ordinates for the proton 4-H and 3-H which would imply a severely distorted ring structure for example r_{34} becomes 2.72 Å ahd r_{45} 2.87 Å. We conclude that the simplified model of ring rotation, *i.e.* fixed geometry and an averaged $\boldsymbol{S}$ matrix, are incompatible with the observed dipolar couplings.

Our data, therefore, suggest that the structure is not likely to be a planar *trans*-form, alone, nor some other single structure with a fixed value of θ, but probably involves an average over θ in which either $\boldsymbol{S}$ or geometry are dependent on θ (or both together). If we assume that changes in $\boldsymbol{S}$ with θ are small, then $V(\theta)$ must have a minimum close to $\theta = 0$ and a large maximum of $\theta = 180°$, as predicted by the molecular orbital calculations.

We hesitate to state with certainty that the liquid and solid state structures do differ by an appreciable amount since the proton spectrum which we have analysed is very complex and the set of D_{ij} values obtained cannot with certainty be taken as a unique set.

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