

On the Structure of 2,2'-Bipyrimidine. Gas and Solid Phase Structure and Barrier to Internal Rotation

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The structure of the title compound was determined in the gas phase by the electron diffraction method and at room temperature by X-ray diffraction methods. The crystal structure of its dihydrate at -158°C was also determined.

The geometry of the pyrimidyl rings was found to be equal to that of pyrimidine. The measured inter-ring bond length is 1.50 \AA . The torsion angle about this bond was found to be 49° in the gas phase using a static model. When a dynamic model was applied, the energy barriers at 0 and 90° in the twist angle were found to be 6.3 and 2.5 kJ mol^{-1} , with the energy minimum at 48° .

In the crystals of 2,2'-bipyrimidine the two rings are apparently bound by symmetry to be parallel. However, the libration about the long axis of the molecule is large, which may correspond to a statistically disordered non-planar molecule. In the dihydrate crystal structure two of the four nitrogen atoms are hydrogen bonded to water molecules. The bipyrimidyl moiety is planar in this structure and lacks an exceptionally large libration.

The structure of biphenyl has been the subject of a number of experimental and theoretical investigations. In the gas and liquid phases, as well as in solution, the torsion angle about the central bond is large ($45 \pm 15^\circ$).^{1–3} This is also the case for the isolated molecule according to theoretical calculations.⁴ In the crystal the molecule was found to be planar.⁵ However, this planarity is claimed to be the result of crystal disorder and might possibly be a consequence of a non-equilibrium situation.⁶

The present investigation of 2,2'-pyrimidine was initiated in order to find out if this molecule would present the same types of problems as biphenyl. We were also interested in learning if the lone pairs of electrons on the nitrogen atoms influence

the geometry of the molecule to the same extent as the *ortho* hydrogen atoms in biphenyl.

The gas phase structure determination by the electron diffraction method was carried out with the intention of finding the probability density function of the inter-ring angle rather than the time average value.

X-Ray diffraction methods were used to examine the structure of the anhydrous form of the compound at room temperature and the dihydrate at -158°C .

EXPERIMENTAL

A sample of 2,2'-bipyrimidine was given to us by Professor Dr. W. Lüttke, Göttingen.

Crystals suitable for the X-ray experiments at room temperature were formed by sublimation. When these crystals were cooled to liquid nitrogen temperature, they disintegrated. Crystals for the low temperature diffraction experiments were grown from an ether–pentane solution at -80°C . These turned out to contain water of crystallization. These crystals disintegrated when brought to room temperature.

Electron diffraction data. The electron diffraction data were recorded with the Oslo apparatus.⁷ The scattering patterns were transferred to intensity data using an integrating densitometer; the data were then treated in the usual way.⁸ An automatic background subtraction program was applied and some of the experimental conditions are given in Table 1. The modification function $s/|f_c||f'_N|$ was used. Experimental data is available upon request.

The elastic scattering factors were calculated by the partial wave methods^{9a} based upon analytical Hartree-Fock potentials for C and N,^{9c} and using the best electron density of bonded hydrogen for H.^{9b} The inelastic scattering factors used were those reported by Tavard *et al.*¹⁰

Table 1. Experimental and refinement conditions for 2,2'-bipyrimidine. Electron diffraction.

Nozzle-to-plate distance (mm)	480.51	200.65
Electron wave length (Å)	0.0646	
Nozzle temperature (°C)	185	
Number of plates	2	2
Degree of polynomial in background subtraction	7	9
Data range (Å ⁻¹)		
s_{\min}	1.50	6.75
s_{\max}	19.00	42.75
Data interval Δs (Å ⁻¹)	0.125	0.25
Constant of the weight scheme ^a		
s_1 (Å ⁻¹)	3.00	8.00
s_2 (Å ⁻¹)	18.00	38.00
w_1 (Å ²)	0.10	0.10
w_2 (Å ²)	0.05	0.05

^a See Ref. 8.

X-Ray data. Data were collected on a SYNTEX PI four-circle diffractometer using graphite crystal monochromatized MoK α radiation ($\lambda=0.71069$ Å). Unit cell dimensions were determined by a least-squares fit to the refined diffractometer settings for 15 general reflections. Details of the experimental conditions are given in Table 2.

The intensities were corrected for Lorentz and polarizations effects; no absorption or extinction corrections were applied. Atomic form factors used were those of Ref. 11 for C, N and O and of Ref. 9b for H.

Crystal data. 2,2'-Bipyrimidine, C₈H₆N₄, monoclinic, $a=3.952(2)$ Å; $b=10.895(8)$ Å; $c=8.844(4)$ Å;

Table 2. Experimental conditions for 2,2'-bipyrimidine and 2,2'-bipyrimidine dihydrate. X-Ray diffraction.

	C ₈ H ₆ N ₄	C ₈ H ₆ N ₄ ·2H ₂ O
Crystal size (mm)	0.1 × 0.1 × 0.3	0.2 × 0.2 × 0.4
Temperature at crystal site (°C)	18	-158
Scanning mode	$\theta/2\theta$	$\theta/2\theta$
Scan speed, depending on intensity (2 θ° min ⁻¹)	1-4	2-3
Scan range (°)	± 1	± 1.2
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.65	0.90
No. of reflections recorded	626	1758
No. of obs. reflections ($\sigma(I) > 2.5I$)	491	1721

$\beta=101.15(4)^\circ$, ($t=18^\circ\text{C}$), $V=373.6$ Å³; $F(000)=164$; $Z=2$; $M=158.16$; $D_x=1.406$ g cm⁻³, $\mu(\text{MoK}\alpha)=1.01$ cm⁻¹. Space group $P2_1/n$ (No. 14).

2,2'-Bipyrimidine dihydrate, C₈H₆N₄·2H₂O, monoclinic, $a=6.859(2)$ Å; $b=4.726(2)$ Å; $c=14.056(3)$ Å; $\beta=100.47(2)^\circ$, ($t=-158^\circ\text{C}$), $V=448.1$ Å³; $F(000)=204$; $Z=2$; $F.W.=194.19$; $D_x=1.439$ g cm⁻³; $\mu(\text{MoK}\alpha)=1.14$ cm⁻¹. Space group $P2_1/n$ (No. 14).

STRUCTURE REFINEMENTS AND RESULTS

Electron diffraction. The analysis in the gaseous state was carried out with the following constraints:

(a) All C-N bond lengths are equal in accordance with the results from the X-ray analysis.

(b) All C-H bond distances are equal.

(c) The pyrimidyl rings have C_{2v} symmetry.

(d) The overall molecular symmetry in the gaseous state is C_2 .

The following structure parameters were used to describe the molecular geometry: $r(\text{C4}-\text{C5})$, $r(\text{C2}-\text{N1})$, $r(\text{C2}-\text{C2}')$, $r(\text{C}-\text{H})$, $\angle\text{N}-\text{C}-\text{N}$, $\angle\text{C}-\text{N}-\text{C}$, $\angle\text{N}-\text{C}-\text{H}$ and $\phi(\text{N1}-\text{C2}-\text{C2}'-\text{N3}')$. The numbering of the atoms are given in Fig. 1.

During the analysis, the torsion angle about the inter-ring bond was treated both as a small and a large amplitude motion.

First the torsional motion was treated conventionally by refining the torsion angle ϕ . This approach corresponds to a small amplitude motion about the equilibrium conformation. In this treatment the l and K values include the contribution from the torsional motion.¹² An estimated modified valence field adjusted to reproduce the most important frequencies has been used for calculation of l , l^{tr} , K and K^{tr} values.

The torsional motion was next treated as a large amplitude motion. In this case the modified molecular intensity is given by:¹³

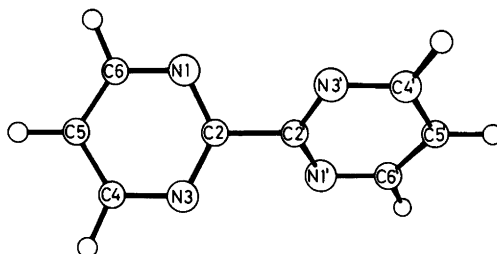


Fig. 1. 2,2'-Bipyrimidine.

Table 3. Final structure parameters for gaseous 2,2'-bipyrimidine.

	Static model ^a r_a (Å), \angle_a (°)	l (Å)	Dynamic model ^b r_a (Å), \angle_a (°)
V_2 (kJ mol ⁻¹)			-2.3(1.2)
V_4 (kJ mol ⁻¹)			-4.8(1.3)
C-C	1.387(1)	0.0465 ^c	1.386(3)
C-N	1.337(1)	0.0460	1.337(2)
C2-C2'	1.511(2)	0.0500	1.505(4)
C-H	1.087(4)	0.0770	1.092(9)
\angle N-C-N	127.4(2)		127.8(2)
\angle C-N-C	115.4(1)		115.2(2)
\angle N-C-H	112.9(10)		113.2(23)
ϕ	49.1(10)		
$l(1\cdots3)$	0.053 (1)		0.054 (2)
$l(1\cdots4)$	0.055		0.056
$l(1\cdots5)$	0.055		0.056
$l(1\cdots2')$	0.072 (2) ^d		0.073 (3) ^d
$l(2\cdots4)$	0.055		0.056
$l(4\cdots6)$	0.055		0.056
$l(1\cdots5')$	0.134 (8)		0.135 (8)
$l(2\cdots4')$	0.065 (3)		0.068 (5)
$l(4\cdots5')$	0.114 (10)		0.115 (8)
R (%)	5.83 ^e		5.34 ^e

^a Standard deviations from the least squares refinement using a diagonal weight matrix. ^b Standard deviations using a non-diagonal weight matrix and including uncertainty in the electron wave length. ^c Fixed according to calculated values. ^d Refined in one group. ^e $R = |\sum w_i \Delta_i^2 / \sum w_i I_i^2(\text{obs})|^{1/2}$, where $\Delta_i = I(\text{obs}) - I(\text{calc})$.

$$I(s) = \text{const.} \sum_{i \neq j=1}^M \sum_{k=1}^M g_{ij/ki}(s) \int P_{ij}(r) \frac{\sin(rs)}{r_{ij}} dr$$

where the probability function is

$$P_{ij}(r) = \int P_{ij}^{\text{fr}}(r, \phi) P(\phi) d\phi$$

and

$$P(\phi) = N \exp(-V(\phi)/RT) \quad (1)$$

N is a normalization constant and $V(\phi)$ is the potential energy distribution for rotation about the C-C bond, taken as

$$V(\phi) = \frac{V_2}{2}(1 - \cos 2\phi) + \frac{V_4}{2}(1 - \cos 4\phi) \quad (2)$$

$P_{ij}^{\text{fr}}(r, \phi)$ is a Gaussian distance distribution for a hypothetical molecule performing harmonic framework vibrations with a fixed ϕ value,¹³ i.e. the contribution from the torsional motion is not included in I_{ij}^{fr} . $P_{ij}^{\text{fr}}(r, \phi)$ is given as

$$P_{ij}^{\text{fr}}(r, \phi) = \frac{(2\pi)^{-1/2}}{I_{ij}^{\text{fr}}(\phi)} \exp - \frac{[r - r_{ij}(\phi)]^2}{2[I_{ij}^{\text{fr}}(\phi)]^2}$$

Because of the symmetry it is sufficient to consider $V(\phi)$ between 0 and 90°. This interval was divided into nine subintervals and the population of each subinterval was calculated according to Eqn. 1. The I_{ij}^{fr} and K_{ij}^{fr} values were calculated for each subinterval.

The final structure parameters for the different approaches are given in Table 3. The correlation matrix corresponding to the dynamic model is given in Table 4. The molecular intensity curve and the radial distribution curve for this model are shown in Figs. 2 and 3, respectively.

Table 4. Correlation matrix corresponding to the dynamic model (larger than 0.50).

V_2/V_4	= 0.67	C4-C5/C-N	= -0.79
C4-C5/CNC	= 0.53	NCN/CNC	= -0.68

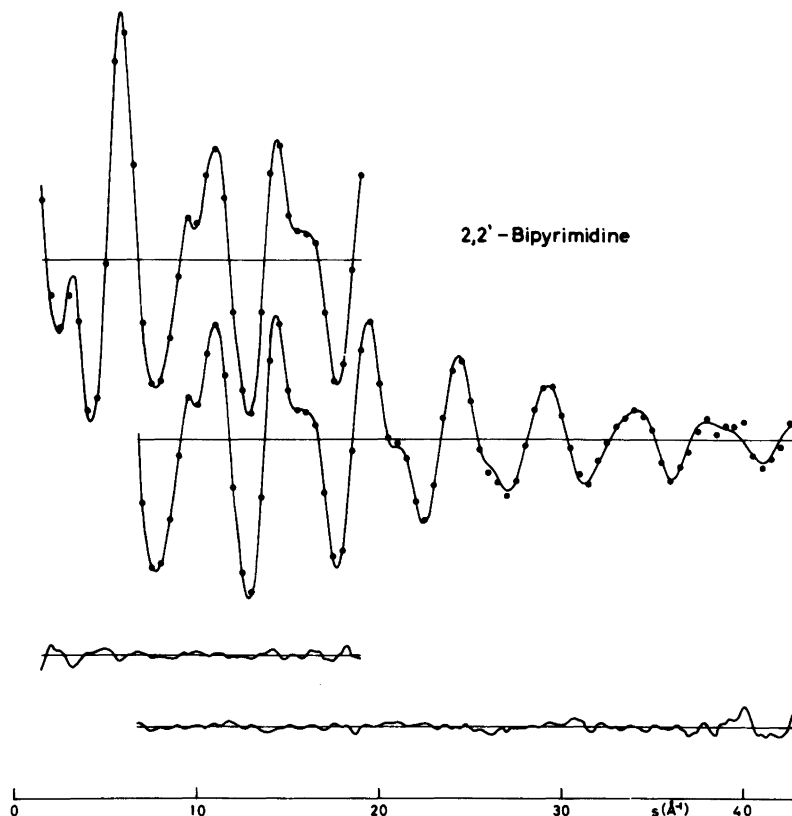


Fig. 2. Experimental (dots) and theoretical (full line) intensity curves, and the difference curves.

X-Ray diffraction. Both crystal structures were determined by direct methods¹⁴ and refined¹⁵ by standard Fourier and full-matrix least-squares methods. Non-hydrogen atoms were given anisotropic thermal parameters, hydrogen atoms were treated isotropically. In order to reduce the effect from bonding electrons, an extra weight function was applied to low-angle data in the least-squares procedure: For 2,2'-bipyrimidine the weights ($\sigma(F)^{-2}$) were multiplied by a function with a value of 0 at $\sin \theta/\lambda = 0 \text{ \AA}^{-1}$ rising to 1 at $\sin \theta/\lambda = 0.4 \text{ \AA}^{-1}$. For the hydrate all reflections with $\sin \theta/\lambda < 0.55 \text{ \AA}^{-1}$ were given zero weight.

Refinements converged to the following residuals: 2,2'-bipyrimidine: $R = 0.050$; $R_w = 0.042$; $S = (\sum w \Delta F^2 / (n - m))^{1/2} = 1.42$, 2,2'-bipyrimidine dihydrate: $R = 0.036$ (for 1149 reflections); $R_w = 0.036$; $S = 1.47$. The final atomic parameters are listed in Table 5. Structure factor tables are available from the

authors.

Rigid-body analyses for the 2,2'-bipyrimidine molecules gave r.m.s. ΔU values of 0.0025 \AA^2 for the room temperature structure and 0.0005 \AA^2 for the hydrate. Eigenvalues of the T-tensors are 0.046, 0.041 and 0.028 \AA^2 and 0.017, 0.015 and 0.012 \AA^2 for the anhydrous and hydrate structures, respectively. For the L-tensors the eigenvalues are 61.2, 14.1 and $6.2(^{\circ})^2$ and 12.63, 1.95 and $1.06(^{\circ})^2$, respectively. In the anhydrous structure the axis of largest libration corresponds to the long axis of the molecule. In the hydrate structure, probably owing to the hydrogen bonding, the axis of largest libration forms an angle of 16° with the long molecular axis.

Structural data for the two crystal forms are listed in Table 6. Estimated standard deviations were obtained from the variance-covariance matrix.

Deviations from the least squares planes through

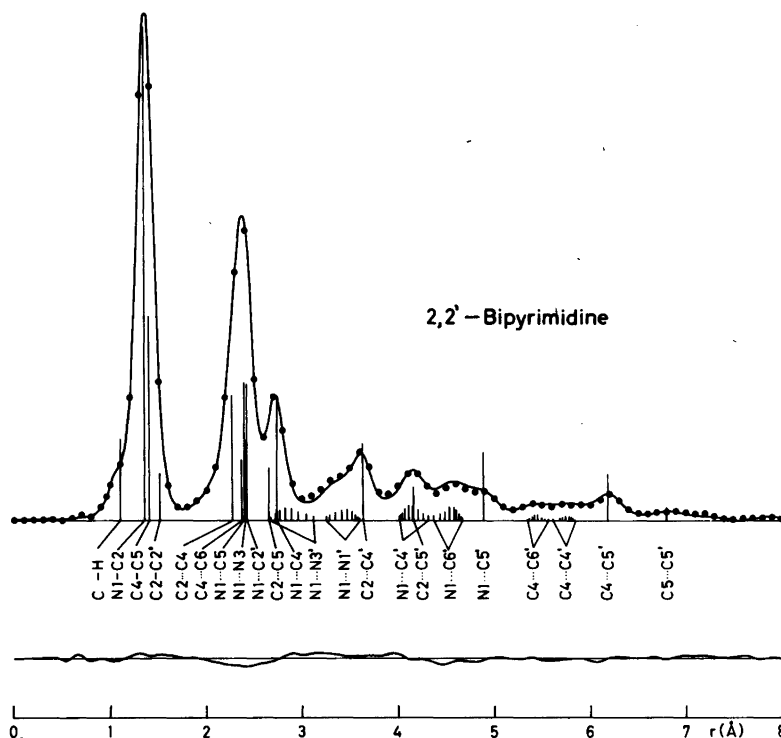


Fig. 3. Experimental (dots) and theoretical (full line) radial distribution functions with an artificial damping constant $B=0.0020 \text{ \AA}^2$. The position and approximate area (length of the bar) of the peaks corresponding to the most important distances are shown together with the distance distribution for some of the torsion dependent distances. Theoretical intensities have been used below $s=1.5 \text{ \AA}^{-1}$.

the six non-hydrogen atoms of one ring and the 12 non-hydrogen atoms of the molecule are listed for both crystal structures in Table 7.

DISCUSSION

Gas phase structure of 2,2'-bipyrimidine. The structural parameters obtained for the molecule in the gaseous state using a static and a dynamic model are given in Table 3. The parameters derived using the two models are identical within the quoted error limits.

The barrier height calculated at 0 and 90° is 6.3 and 2.5 kJ mol^{-1} , respectively, with an energy minimum, $\phi_{\min}=1/2 \arccos(-V_2/4V_4)=48.4^\circ$. A potential function of the form; $V(\phi)=\sum_{i=0}^5 a_i \phi^i$ was also examined, where the barrier heights at 0 and 90° as well as ϕ_{\min} were refined together with the

other structure parameters. In order to determine all the a_i 's the following constraints were used;

$$\left. \frac{dV}{d\phi} \right|_{\phi=0^\circ} = \left. \frac{dV}{d\phi} \right|_{\phi=90^\circ} = V(\phi_{\min}) = 0.$$

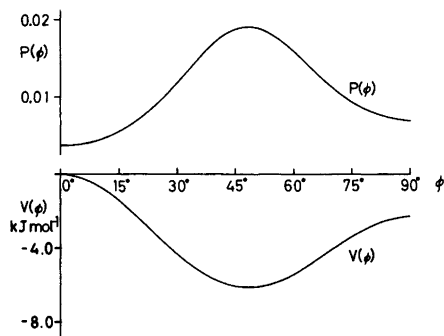


Fig. 4. Potential energy distribution curve, $V(\phi)$, and the probability density distribution, $P(\phi)$.

Table 5. Fractional atomic coordinates and thermal parameters with estimated standard deviations for (A) 2,2'-bipyrimidine and (B) 2,2'-bipyrimidine dihydrate. The anisotropic temperature factor is given as $\exp -2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{12}a^*b^*hk + \dots)$.

A									
Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N1	.4222(6)	.1540(2)	.4265(2)	.0743(15)	.0334(10)	.0580(13)	.0037(9)	.0184(11)	.0053(9)
N3	.6487(5)	-.0212(2)	.3223(2)	.0683(14)	.0440(12)	.0460(11)	.0031(10)	.0170(10)	.0004(9)
C2	.5205(6)	.0365(2)	.4306(2)	.0419(12)	.0353(11)	.0406(11)	-.0035(10)	.0041(9)	-.0035(9)
C4	.6847(7)	.0471(3)	.2006(3)	.0759(19)	.0645(16)	.0455(14)	.0023(15)	.0198(13)	.0030(14)
C5	.5936(7)	.1678(3)	.1851(3)	.0672(19)	.0654(18)	.0550(16)	-.0049(14)	.0152(15)	.0215(15)
C6	.4605(8)	.2164(2)	.3012(3)	.0757(20)	.0415(14)	.0726(18)	.0016(13)	.0173(15)	.0147(14)
B									
Atom	x	y	z	B	Atom	x	y	z	B
HC4	.779(7)	.003(2)	.125(3)	5.3(6)	HC5	.626(6)	.213(2)	.104(3)	5.0(6)
HC6	.393(7)	.297(3)	.297(3)	5.6(6)					
B									
Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	.7104(1)	.6208(1)	.6979(1)	.0276(3)	.0182(3)	.0199(2)	.0035(2)	.0082(2)	-.0009(2)
N1	.7462(1)	.6158(1)	.4870(0)	.0161(2)	.0162(2)	.0202(3)	.0011(2)	.0058(2)	.0007(2)
N3	1.0068(1)	.7533(2)	.4047(1)	.0203(3)	.0184(3)	.0192(3)	.0037(2)	.0084(2)	.0040(2)
C2	.9318(1)	.6024(2)	.4700(0)	.0158(3)	.0135(2)	.0149(2)	.0013(2)	.0049(2)	-.0004(2)
C4	.8823(1)	.9354(2)	.3514(1)	.0232(3)	.0196(3)	.0193(3)	.0043(2)	.0069(2)	.0043(2)
C5	.6857(1)	.9632(2)	.3615(1)	.0205(3)	.0189(3)	.0190(3)	.0037(2)	.0027(2)	.0013(2)
C6	.6234(1)	.7939(2)	.4313(1)	.0167(3)	.0169(3)	.0216(3)	.0016(2)	.0042(2)	-.0005(2)
B									
Atom	x	y	z	B	Atom	x	y	z	B
HC4	.957(9)	1.058(12)	.304(4)	3.5(7)	HC5	.606(6)	1.101(9)	.330(3)	2.5(5)
HC6	.473(8)	.789(10)	.447(3)	3.0(6)	HO1	.730(7)	.575(10)	.640(3)	2.8(6)
HO2	.734(7)	.476(11)	.727(3)	2.7(5)					

Unfortunately the barrier height calculated at 0° had a standard deviation larger than the barrier itself. When the barrier at 0° was fixed at 6.2 kJ mol $^{-1}$, ϕ_{\min} and $V(\phi=90^\circ)$ refined to 46(6) $^\circ$ and 3(1) kJ mol $^{-1}$, respectively, in good agreement with the results obtained from the Fourier expansion of the potential.

The potential energy distribution, $V(\phi)$, for rotation about the central C-C bond based on a Fourier expansion (Eqn. 2) is shown in Fig. 4 together with the corresponding probability function, $P(\phi)$ (Eqn. 1). The torsional overtone ($\Delta v=2$) for biphenyl is observed at 55.4 cm $^{-1}$. An estimate of the torsional force constant from the potential energy distribution and comparison to the torsional force constant for biphenyl indicates a slightly smaller torsional frequency for 2,2'-bipyrimidine. Assuming a torsional frequency of 25 cm $^{-1}$ for 2,2'-bipyrimidine the energy of the torsional ground

state is only 150 J mol $^{-1}$. If the torsional excited vibrational states are populated according to a Boltzmann distribution, about 74% of the molecules are below the lowest energy barrier of 2.5 kJ mol $^{-1}$ at the experimental temperature of 185 $^\circ$ C. This should justify the use of a large amplitude model.

Recent *ab initio*¹⁶ calculations on 2,2'-bipyrimidine determined the values of $V(\phi=0^\circ)$, $V(\phi=90^\circ)$ and ϕ_{\min} to be 0.88, 1.36 kcal mol $^{-1}$ and 40° , respectively. The calculated barriers are of the same order of magnitude as the experimentally derived values, however, the *ab initio* calculation gave a higher barrier at 90° than at 0° . This is also the case for biphenyl⁴ where *ab initio* calculations give values of 1.2 and 4.5 kcal mol $^{-1}$ and 32° for $V(\phi=0^\circ)$, $V(\phi=90^\circ)$ and ϕ_{\min} , respectively. In both cases the calculated value for ϕ_{\min} is smaller than the experimental value by approximately 8–10 $^\circ$

Table 6. Structural data for (A) 2,2'-bipyrimidine and (B) 2,2'-bipyrimidine.2H₂O as obtained from the crystal structure determination.

			A	corr.	B	corr.
Bond lengths (Å)						
N1	C2		1.336(3)	1.349	1.339(1)	1.341
N1	C6		1.334(3)	1.338	1.338(1)	1.339
N3	C2		1.326(3)	1.338	1.336(1)	1.339
N3	C4		1.338(3)	1.342	1.341(1)	1.342
C2	C2'		1.497(4)	1.502	1.496(1)	1.497
C4	C5		1.363(4)	1.376	1.388(1)	1.389
C5	C6		1.349(4)	1.360	1.393(1)	1.395
C4	HC4		0.96(3)		1.08(6)	
C5	HC5		0.90(3)		0.91(4)	
C6	HC6		0.92(3)		1.09(3)	
O	HO1				0.88(5)	
O	HO2				0.80(5)	
Bond angles (°)						
N1	C2	C2'	117.0(2)		116.5(1)	
N3	C2	C2'	117.3(2)		117.0(1)	
N1	C2	N3	125.7(2)		126.5(1)	
C2	N3	C4	115.6(2)		116.1(1)	
N3	C4	C5	123.4(3)		122.4(1)	
C4	C5	C6	115.8(3)		116.5(1)	
C5	C6	N1	123.8(3)		122.2(1)	
C6	N1	C2	115.6(2)		116.3(1)	
N3	C4	HC4	113(2)		111(3)	
C5	C4	HC4	123(2)		126(3)	
C4	C5	HC5	122(2)		122(3)	
C6	C5	HC5	122(2)		121(3)	
C5	C6	HC6	120(2)		125(2)	
N1	C6	HC6	116(2)		113(2)	
HO1	O	HO2			102(4)	
Hydrogen bonds in B						
O-N1 (Å)	3.018(1)	HO1-N1 (Å)	2.18(5)		∠O-OH1-N1 (°)	160
O-O* (Å)	2.782(1)	HO2-O* (Å)	1.98(5)		∠O-OH2-N2 (°)	180 [‡]
* -x + 1½, y - ½, -z + 1½						

which suggests that the barrier at 90° may be overestimated by the *ab initio* calculations.

The torsion of biphenyl¹⁷ has been studied in the gaseous state by Raman spectroscopy. The Fourier coefficients V_2 and V_4 were determined for different values of ϕ_{\min} . The experimental results are consistent with the barrier at 0° being larger than the one at 90°, if $\phi_{\min} > 45^\circ$. For $\phi_{\min} = 50^\circ$, the V_2 and V_4 values determined for biphenyl are -1.0 and -1.5 kcal mol⁻¹, respectively.

Crystal structure of 2,2'-bipyrimidine (anhydrous form). The molecules lie on crystallographic centres

of symmetry with the two pyrimidyl rings of each molecule coplanar. The libration about the long axis of the molecule is fairly large, corresponding to an r.m.s. oscillation of 7.8°. Comparable values were found for biphenyl at room temperature (10.3°) and at 110 K (6.8°).⁶ The large libration for biphenyl has been interpreted as possibly being a statistically-centred arrangement for the molecule with the two phenyl rings independently rotating around the single bond in a double minimum potential.⁶ The same may be the case for the pyrimidyl rings in the present structure, but the

Table 7. Deviations (Å) from least-squares planes (I) through carbon and nitrogen atoms of one ring and (II) of both rings for (A) 2,2'-bipyrimidine and (B) the dihydrate.

	A		B	
	I	II	I	II
N1	0.002	-0.001	0.010	0.016
N3	-0.006	-0.009	-0.005	0.001
C2	0.005	0.000	-0.004	0.005
C4	0.003	0.003	0.008	0.007
C5	0.004	0.007	-0.001	-0.007
C6	-0.008	-0.007	-0.009	-0.010
HC4	0.000	0.001	0.075	0.071
HC5	0.041	0.046	0.105	0.094
HC6	-0.012	-0.010	-0.031	-0.034

fact remains that the torsion angle about the inter-ring bond is much smaller in the solid than the gas phase.

The packing of the molecules is of the usual plane to plane stacking type with an interplanar separation of 3.36 Å. The arrangement is shown in Fig. 5A.

In order to investigate further the possibility of orientational disorder, a calculation of the sum of intermolecular potentials in the crystal was performed for a rotation about the long molecular axis. These calculations were performed using a computer program by Shmueli and Goldberg.¹⁸ The libration potential was constructed both for the whole molecule and for one pyrimidyl moiety keeping the other half of the molecule stationary. In the latter case, non-bonded interactions between the two pyrimidyl moieties such as N-N potentials were also included in the calculation and may

simulate an oscillation about the central bond of the rings in opposite phase.

The calculation including the whole molecule resulted in a libration potential with a half width at kT over the minimum, of 6.9°, which is in good agreement with the experimental r.m.s. libration of 7.8°. The corresponding half width, when only one half of the molecule was included in the calculations, was 10.9°, and there was no indication of a double minimum. The absence of a double minimum may indicate that the N-N repulsion is negligible compared to the gain in van der Waals packing forces and that the molecule is essentially planar in the crystal at room temperatures.

Crystal structure of 2,2'-bipyrimidine dihydrate. In these crystals the molecules are also situated on centres of symmetry. One of the nitrogen atoms in each ring is engaged in a hydrogen bond to a water molecule. The water molecules are also hydrogen bonded to each other; see Table 6. The 2,2'-bipyrimidine molecules are stacked as shown in Fig. 5B.

The libration of this molecule does not show any exceptional features. The largest r.m.s. oscillation is 3.6° about a direction not far from the long molecular axis. One must therefore conclude that this 2,2'-bipyrimidine molecule is planar.

Comparison of the structures. Listed in Table 8 are the mean structural data for the pyrimidyl moiety; two-fold symmetry was assumed about the C2...C5 diagonal as well as equal C-N bond lengths. This is consistent with the structural data obtained for pyrimidine²⁰ and 2,2'-bipyrimidine in the solid state. A significant difference is found between the N-C-N angle in the gas phase and that determined for the solid phases; it is approximately 1° larger in the gas phase. The inter-ring

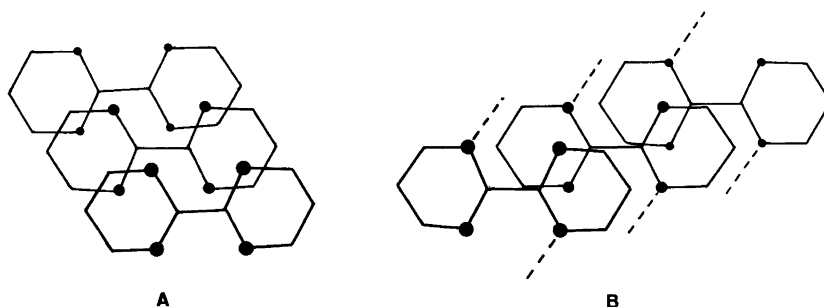


Fig. 5. Packing arrangement of (A) 2,2'-bipyrimidine and (B) 2,2'-bipyrimidine. In (B) dotted lines indicate hydrogen bonds.

Table 8. Comparison of structural data for pyrimidine and 2,2'-bipyrimidine, assuming two-fold symmetry about C2–C5 and equal C–N bonds.

	Pyrimidine ED, gas phase ¹⁹	Pyrimidine X-ray, ²⁰	2,2'-Bi- pyrimidine ED, gas phase	2,2'-Bi- pyrimidine X-ray, 18 °C	2,2'-Bi- pyrimidine, dihydrate, X-ray, –158 °C
C–C (Å) intra-ring	1.393(2)	1.391(2)	1.386(3)	1.369(4)	1.392(1)
C–N (Å)	1.340(2)	1.339(2)	1.337(3)	1.342(3)	1.340(1)
C–C (Å) inter-ring			1.505(4)	1.502(4)	1.497(1)
C–H (Å)	1.099(7)	0.97(3) ^a	1.092(9)	0.93(3) ^a	1.03(5) ^a
∠NCN (°)	127.6(3)	126.8(1)	127.8(2)	126.1(2)	126.5(1)
∠CNC (°)	115.5(2)	116.1(1)	115.2(2)	115.4(2)	116.2(1)
∠NCH (°)	115(3)	114(2)	113(2)	115(2)	112(3)

^a X-Ray diffraction usually provides C–H bond lengths that are short.

C–C bond was found to be slightly, but not significantly, longer in the gas state than in the solids. This is brought about by the difference in the inter-ring dihedral angle for the two states; the conjugation in a planar system would enhance the double bond character of the inter-ring bond and correspondingly decrease the N–C–N angle.

The largest difference between the structure of the free 2,2'-bipyrimidine molecule and the molecule in the crystal states resides, as in biphenyl, in the dihedral angle between the rings. The minimum potential for the free molecule is at an inter-ring angle close to that of biphenyl, which suggests that a nitrogen lone pair in this type of compound demands about the same space as a hydrogen atom.

Though in the solid the inter-ring torsion angle was found to be zero, the molecule may not be planar in the usual sense of the word. Intermolecular forces must in part, be responsible for the stabilization of the planar model in the solid state.

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