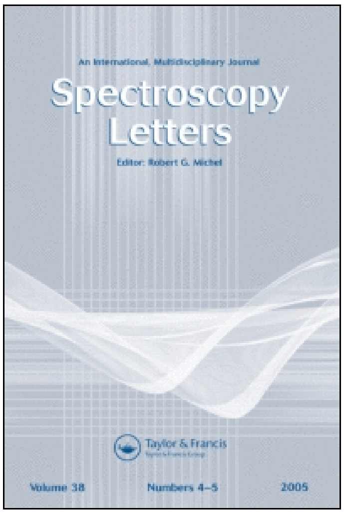

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Structure and Conformation of 4,4'-Bipyridine

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STRUCTURE AND CONFORMATION OF 4,4'-BIPYRIDINE

Keywords : Structure, crystal, conformation, bipyridine, AM1.

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ABSTRACT

The title compound has been investigated by x-ray analysis and AM1 semi-empirical quantum mechanical method. The geometry of the two molecules in the asymmetric unit is different in terms of the torsion angle θ [C4-C5-C6-C10] between the two pryidine rings which is -34.1 (2)° and -17.9 (2)° in molecule I and II respectively. The conformation of the energy profile showed that the minimum energy conformation has the torsion angle θ near 35°. The crystal structure is stabilized by C-H ... N hydrogen bonds.

INTRODUCTION

The stereochemistry of the 4,4'-bipyridine molecule has been the subject of some experimental and theoretical studies. It is known that the molecule is non-planar in the vapour phase because of the steric repulsion of the ortho hydrogen atoms. It is found that the torsion angle about C-C' is 37.2 ° in the vapour phase[1] . The assignments on the IR and Raman spectra of the molecule in the solid phase and the normal coordinate analysis have been reported to be in accord with the centrosymmetric and planar structure with the symmetry D_{2h}[2,3].

The present study of bipyridine has been undertaken in order to investigate the conformational and crystallographic analysis of the molecule in the solid phase.

EXPERIMENTAL

4,4'-bipyridine crystals were obtained by slow evaporation of an aqueous solution at room temperature.

Intensity measurements for crystal structure analysis were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer operating in the $\omega/2\theta$ scanning mode using suitable crystals for data collection. Unit cell constants were obtained by least-squares analysis of 25 well-centered reflections in the ranges $5° < \theta < 10°$. The measurements were carried out up to $2\theta_{max} = 52.0°$. During data collection three standard reflections periodically observed and showed no significant intensity variations (% 5.4). The ranges of h,k,l are $-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$. 3295 unique reflections were measured of which 2624 had $I > 2\sigma(I)$. Corrections for Lorentz and polarization were applied to the intensity values. These observed reflections were used for structure determination and refinement. The structure was determined by direct methods (MULTAN - MolEN)[4] and refined full-matrix least squares methods (LSFM - MolEN)[4]. The function minimized was $\sum w(|Fo|-|Fc|)^2$. All non-H atoms were refined with anisotropic thermal parameters. H-atoms were placed geometrically 0.95 Å from the corresponding C atoms. For all H-atoms a riding model was used with $U_{iso}(H) = 1.3\ U_{eq}(C)$. The final R and R_w values are given in Table 1. The final difference map showed maximum and minimum peaks of 0.11 (3), -0.15 (0) e/Å^3. Table 1. shows the crystal and relevant x-ray data.

RESULTS AND DISCUSSION

The structure of two molecules in the asymmetric unit is shown in Fig.1. The fractional coordinates and mean temperature factors with estimated standard

TABLE 1.
Crystal and relevant x-ray data

Formula	$C_{10}N_2H_8$
Crystal system	triclinic
Space group	$P\bar{1}$
Mol. Wt.	156.189
Crystal size (mm)	0.60x0.40x0.20
a(Å)	8.830(2)
b(Å)	8.894(1)
c(Å)	11.024(2)
α (°)	85.48(2)
β (°)	85.41(1)
γ (°)	77.78(3)
V($Å^3$)	841.7(3)
D_c($g.cm^{-3}$)	1.232
μ (mm^{-1})	0.705
Z	4
λ (MoK_α) (Å)	0.7103
Nuniq	3295
Nobs	2624
Variables	217
R	0.0414
Rw	0.0486
$\Delta\rho_{max}$	0.112
$\Delta\rho_{min}$	-0.152

deviations for non hydrogen and hydrogen atoms participating in hydrogen bonds are listed in Table 2 and the selected geometric parameters are given in Table 3.

Bond distances and angles of the pyridine rings are in agreement with the values in the literature[5,6]. The geometry of the molecules in the two polymorphs is identical within experimental error for both bond lengths and angles. The more striking difference between the two molecules in the polymorph described here is seen in the torsion angle C4-C5- C6-C10 between the two pyridine rings; this angle is -34.1 (2)° in the molecule I and -17.9 (2)° in the molecule II, which is more planar. The great

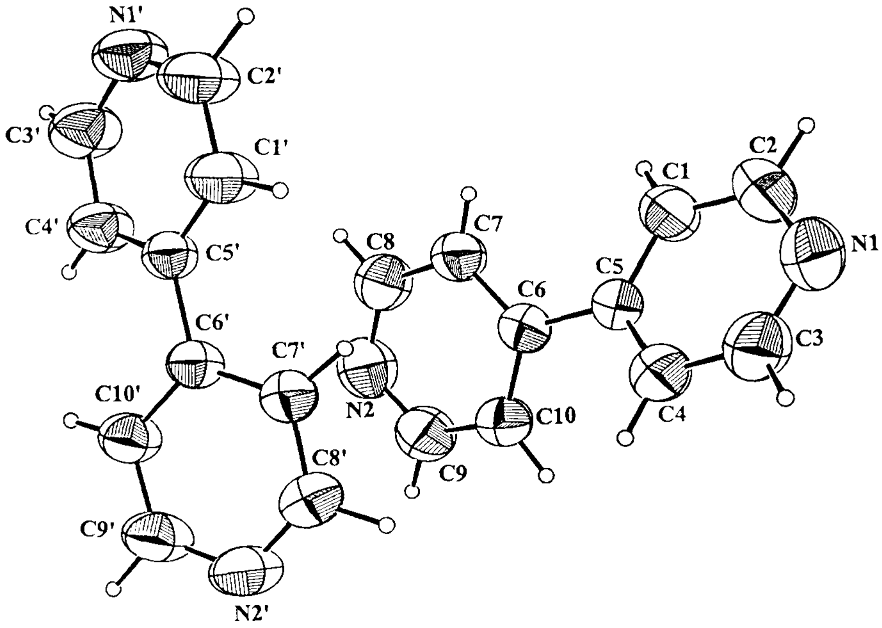

Figure 1. An ORTEP drawing of the title compound with the atomic labelling. The displacement ellipsoids are drawn at the 50% probability level

length of the bond linking the two pyridine rings [1.484(2) and 1.492(2) for the molecule I and II respectively] indicates that there is no conjugation between the rings. In 3,3'-dimethyl-4,4'-bipyridine, the C5-C6 bond length is 1.508 (6)Å indicating single-bond character. The pyridine rings are planar within experimental errors, but the 4,4'-bipyridine molecule is not planar. The dihedral angles between the two pyridine planes are 34.66 (8)° for molecule I and 18.60 (14)° for molecule II. Distortions of the rings from planarity are comparable with those in other bipyridine compounds[6,7,8].

The crystal structure of the title compound is stabilized by C-H ... N hydrogen bonds. The symmetry - independent bipyridine molecules are bridged by C7'-

TABLE 2.

Fractional atomic coordinates and B_{eq} values (Å^2) for non-hydrogen atoms and H-atoms participating in hydrogen bonds with e.s.d.s in parentheses.

	x	y	z	B_{eq}
(I)				
N1	0.3188(2)	0.4433(2)	0.3901(1)	6.37(4)
N2	0.7065(2)	-0.0429(2)	0.8588(1)	6.38(4)
C1	0.3275(2)	0.3398(2)	0.5973(1)	5.05(3)
C2	0.2554(2)	0.4305(2)	0.5033(2)	6.06(4)
C3	0.4613(2)	0.3610(2)	0.3705(2)	6.09(4)
C4	0.5423(2)	0.2648(2)	0.4572(1)	5.04(3)
C5	0.4753(2)	0.2526(2)	0.5745(1)	4.06(3)
C6	0.5568(2)	0.1505(2)	0.6722(1)	4.10(3)
C7	0.5370(2)	0.1902(2)	0.7924(1)	4.93(3)
C8	0.6136(2)	0.0921(2)	0.8801(2)	5.89(4)
C9	0.7249(2)	-0.0792(2)	0.7431(2)	6.12(4)
C10	0.6553(2)	0.0116(2)	0.6480(1)	4.98(3)
(II)				
N1'	0.7420(2)	0.5002(2)	1.1107(1)	6.71(4)
N2'	1.1475(2)	0.0216(2)	0.6524(1)	6.05(3)
C1'	0.8012(2)	0.4489(2)	0.9006(2)	6.14(4)
C2'	0.7218(2)	0.5342(2)	0.9933(2)	7.31(5)
C3'	0.8476(2)	0.3759(2)	1.1353(2)	6.94(5)
C4'	0.9335(2)	0.2834(2)	1.0497(1)	5.82(4)
C5'	0.9102(2)	0.3181(2)	0.9282(1)	4.08(3)
C6'	0.9955(2)	0.2184(2)	0.8318(1)	4.07(3)
C7'	0.9420(2)	0.2269(2)	0.7162(1)	4.80(3)
C8'	1.0200(2)	0.1273(2)	0.6315(2)	5.71(4)
C9'	1.2002(2)	0.0176(2)	0.7624(2)	6.00(4)
C10'	1.1301(2)	0.1115(2)	0.8538(1)	5.20(4)
H1'	0.777	0.484	0.815	7.8*
H7'	0.847	0.297	0.692	6.1*

$B_{eq}=(8\pi^2/3)\Sigma_i\Sigma_j U_{ij}\, a_i{}^*a_j{}^*a_ia_j$

TABLE 3.
Bond lengths (Å) and angles (°) with e.s.d.s in parentheses

(I)			(II)		
C4	C3	1.369(2)	C4'	C3'	1.375(2)
C6	C10	1.385(2)	C6'	C10'	1.383(2)
N2	C8	1.330(2)	N2'	C8'	1.332(2)
N2	C9	1.326(2)	N2'	C9'	1.328(2)
N1	C2	1.332(2)	N1'	C2'	1.326(2)
N1	C3	1.328(2)	N1'	C3'	1.311(2)
C10	C9	1.376(2)	C10'	C9'	1.380(2)
C7	C6	1.388(2)	C7'	C6'	1.389(2)
C1	C2	1.372(2)	C1'	C2'	1.378(2)
C7	C8	1.371(2)	C7'	C8'	1.378(2)
C5	C4	1.387(2)	C5'	C4'	1.371(2)
C5	C6	1.484(2)	C5'	C6'	1.492(2)
C5	C1	1.387(2)	C5'	C1'	1.376(2)

C6	C5	C1	120.9(1)	C6'	C5'	C1'	121.6(1)
C5	C4	C3	119.3(1)	C5'	C4'	C3'	119.7(1)
C7	C6	C5	121.1(1)	C7'	C6'	C5'	121.4(1)
C7	C6	C10	117.2(1)	C7'	C6'	C10'	116.8(1)
C5	C6	C10	121.7(1)	C5'	C6'	C10'	121.7(1)
C8	N2	C9	115.9(1)	C8'	N2'	C9'	115.9(1)
C2	N1	C3	115.9(1)	C2'	N1'	C3'	115.1(1)
C6	C10	C9	118.7(1)	C6'	C10'	C9'	119.1(1)
C5	C1	C2	118.6(1)	C5'	C1'	C2'	119.4(1)
C4	C3	N1	124.2(1)	C4'	C3'	N1'	124.9(1)
C7	C8	N2	124.3(1)	C7'	C8'	N2'	123.9(1)
N1	C2	C1	124.7(1)	N1'	C2'	C1'	124.5(1)
N2	C9	C10	124.7(1)	N2'	C9'	C10'	124.6(1)
C6	C7	C8	119.2(1)	C6'	C7'	C8'	119.6(1)
C4	C5	C6	121.8(1)	C4'	C5'	C6'	122.0(1)
C4	C5	C1	117.2(1)	C4'	C5'	C1'	116.4(1)

TABLE 4
Hydrogen bond geometry

D-H...A	D...A	D-H	H...A	<D-H...A	Symmetry
C7’-H7’...N1	3.509(2)	0.976(2)	2.598(2)	155.4(1)	-x+1,-y+1,-z+1
C1’-H1’...N1	3.456(3)	0.996(3)	2.468(1)	171.5(1)	-x+1,-y+1,-z+1

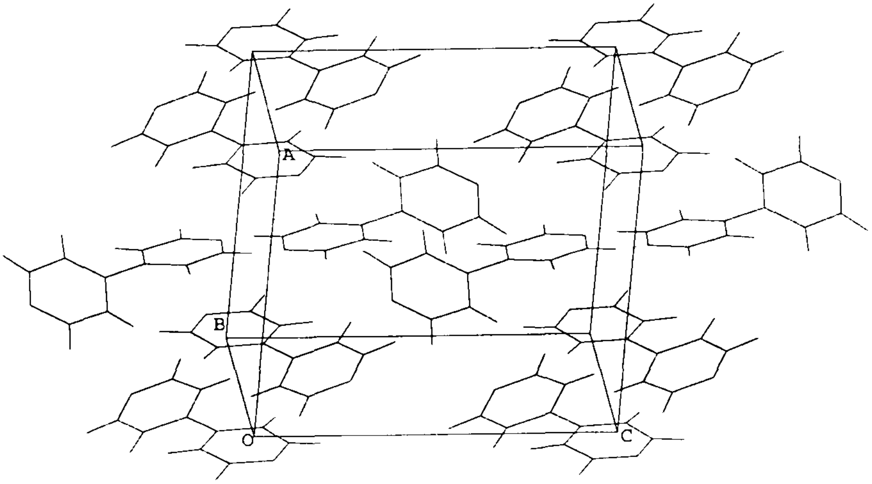

Figure 2. Packing of the molecules in the crystal

H7’...N1 and C1’-H1’...N1 hydrogen bonds. The details of the intermolecular H-bonds are given in Table 4. and the packing diagram is shown in Fig.2.

In order to optimize the geometry and to study the conformation of the isolated molecule of the bipyridine the semi empirical method AM1^{9}, was used. Two molecules occupying the independent part of the unit cell were compared by calculating their single-point energies. The energy difference was 0.04 kcal.mol^{-1} for calculations performed at AM1 level. In all these calculations, the molecule I and II at lower energy is twisted 30° from planarity.

TABLE 5.

Average calculated bond lengths (Å), angles and torsion angles (°)with the average experimental values

	X-ray	AM1
C5-C6	1.484 (2)	1.460
N1-C2	1.332 (2)	1.347
N1-C3	1.328 (2)	1.347
N2-C8	1.330 (2)	1.347
N2-C9	1.326 (2)	1.347
C1-C1-C6	120.9 (1)	120.7
C7-C6-C5	121.1 (1)	121.5
C2-N1-C3	115.9 (1)	117.1
C8-N2-C9	115.9 (1)	117.1
C1-C5-C6-C7	-34.2 (2)	-36.8
C4-C5-C6-C7	146.1 (2)	146.1
C1-C5-C6-C10	145.7 (2)	141.0
C4-C5-C6-C10	-34.1 (2)	-36.1

Selected geometric parameters calculated by the AM1 method are given in Table 5 together with the experimental values. As shown in Table 5, the theoretically obtained geometry for the lowest conformer agrees completely with the geometry of molecule I obtained from x-ray method.

To determine the conformational energy profile, total energy was calculated as a function of the θ torsion angle about the C6-C5 bond. The calculated energy values depending on the θ are given in Table 6 and energy profile for rotation about C4-C5-C6-C7 is shown in Fig.3. Minimum energy conformation has the torsion angle θ near 35° which is good agreement with the structural results for molecule I . Its non-planar conformation is a result of the steric repulsion between the orthohydrogen atoms H1 and H7 and between the orthohydrogen atoms H4 and H10; this steric overcrowding is enough to offset the resonance energy lost by such non

TABLE 6.
The calculated energy depending on θ [C4-C5-C6-C7]

θ (°)	E (kcal/mol) AM1 I	II
0	69,65	69,62
30	68,26	68,22
60	68,58	68,56
90	69,04	69,02
120	68,58	68,54
150	68,22	68,22
180	69,62	69,63

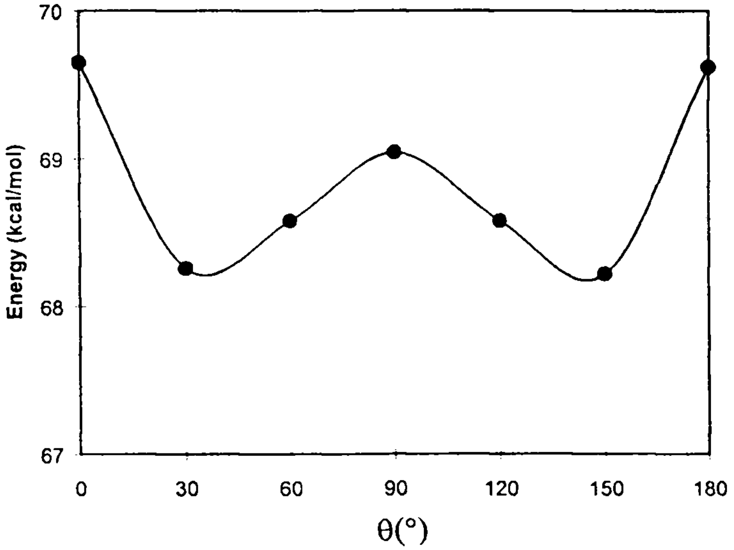

Figure 3. The energy profile for rotation about C4-C5-C6-C7

TABLE 7.
Conformation of 4,4'-Bipyridine for different methods

					This work	
	Electron diff.	NMR	Ab initio STO-3G	Semi emp. NDDO	X-ray	Semi emp. AM1
θ (°)	37.2	29.6	40.8	40	-34.2(2)	30
C-C' (Å)	1.47	-	1.50	1.50	1.484(2)	1.460

planarity. The distances between orthohydrogen atoms are H4-H10 = 2.435 (1)Å, H1-H7 = 2.342 (1)Å for molecule I and H1'-H7'= 2.189(1) Å, H4'-H10'=2.190 (1) Å for molecule II. The distances for molecule I are approximately 0.55 Å greater than the distances obtained from the planar molecule and near the van der Waals separations between hydrogen atoms. For molecule II, the distance is about 0.2 Å shorter than the average value of the van der Waals separations between hydrogen atoms as is shown in biphenyl structure[10]. That steric repulsion increases the separation between C5-C6 beyond the value it would have in an unstrained molecule.

The electron diffraction, proton nuclear magnetic resonance and some theoretical studies have also been undertaken to determine the θ torsional angle of 4,4'-bipyridine in the ground state, all other geometrical parameters being kept fixed[11]. These results are summarized in Table 7 together with the results of this work for molecule I.

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