O1*C*—C1*C*—C2*C*—C4*C*	−179.6 (3)
O1*D*—C1*D*—C2*D*—C4*D*	173.8 (3)
O1*D*—C1*D*—C2*D*—C3*D*	−61.2 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*A*···O2*B*$^{\rm i}$	0.93 (3)	1.98 (3)	2.861 (2)	158 (2)
N1*A*—H2*A*···O3*A*$^{\rm i}$	0.95 (3)	1.84 (3)	2.763 (2)	163 (2)
N1*A*—H3*A*···O1*A*	0.93 (3)	2.00 (3)	2.610 (2)	122 (2)
N2*A*—H4*A*···O3*B*$^{\rm ii}$	0.89 (3)	2.00 (3)	2.886 (2)	176 (2)
N1*B*—H1*B*···O2*A*$^{\rm i}$	0.89 (3)	1.96 (3)	2.762 (2)	148 (2)
N1*B*—H2*B*···O3*B*$^{\rm iii}$	0.93 (3)	1.88 (3)	2.749 (2)	154 (2)
N1*B*—H3*B*···O1*C*	1.02 (3)	1.74 (3)	2.715 (3)	159 (2)
N2*B*—H4*B*···O3*A*	0.95 (3)	1.94 (3)	2.862 (2)	165 (2)
O1*C*—H1*C*···O1*D*	0.90 (4)	1.81 (4)	2.697 (3)	168 (4)
O1*D*—H1*D*···O2*B*$^{\rm iii}$	0.88 (4)	1.83 (4)	2.707 (2)	174 (4)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x - 1, y, z$; (iii) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

The data collection nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures, with the detector set at $2\theta = 29°$. Each set had a different φ angle for the crystal and each exposure covered 0.6° in ω. The crystal-to-detector distance was 4.99 cm. Coverage of the unique set is over 99% complete to 50° in 2θ. Positional parameters were refined for H atoms bonded to O or N, while other H atoms were placed geometrically and refined with constraints to keep all C—H distances and all C—C—H angles on one C atom the same. $U_{\rm iso}$ values were set at $1.2U_{\rm eq}$ of the carrier atom, or at $1.5U_{\rm eq}$ for amino, methyl and hydroxyl groups. Free rotation about C—C bonds was also permitted for methyl groups.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1994). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

The purchase of the Siemens SMART diffractometer was made possible through support from The Research Council of Norway (NFR).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1518). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 672–674

4,4′-Bipyridyl at 203 K

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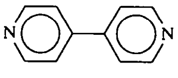
(*Received 10 August 1998; accepted 3 December 1998*)

Abstract

The crystal structure of 4,4′-bipyridyl, $C_{10}H_8N_2$, at 203 K contains two independent, non-planar, molecules whose mean planes subtend an angle of 14.1 (8)°. The long axes of the two molecules are oriented at approximately 88° to each other, allowing interaction between the N atoms and phenyl-H atoms on adjacent molecules and thereby giving rise to a sheet structure. The two molecules are primarily differentiated by the dihedral angle between the connected phenyl rings [18.50 (12) and 34.85 (10)°].

Comment

Although the crystal structure of the 4,4′-bipyridyl molecule, (I), has been reported many times in the context of acting as a Lewis base (*e.g.* Blake *et al.*, 1997; Lu *et al.*, 1997), or cocrystallized with hydrogen donors such as alcohols (Coupar *et al.*, 1996; Sharma & Zawarotko, 1996) or transition metal complexes (Blake *et al.*, 1997; Lu *et al.*, 1997) to form macromolecular arrays (Coupar *et al.*, 1996; Sharma & Zawarotko, 1996), the structure of the molecule itself has only been determined by electron diffraction (Almenningen & Bastiansen, 1958), although the structure of 3,3′-dimethyl-4,4′-bipyridyl has been reported (Gourdon, 1993).



(I)

The major difference between the two independent molecules found in the asymmetric unit is the dihedral angle subtended by the phenyl groups across the connecting C—C bond [18.50 (12)° in molecule 1 and 34.85 (10)° in molecule 2]. This angle was determined to be 37.2° in the gas phase and 48.6° from the latest theoretical calculations (Ould-Moussa *et al.*, 1996). In the sterically congested 3,3′-dimethyl-4,4′-bipyridyl the angle is 81.1° (Gourdon, 1993). In all other respects, the two independent molecules are very similar in their bonds lengths and angles. The C—N bonds are some 0.04 Å shorter than the ring C—C bonds and the angle

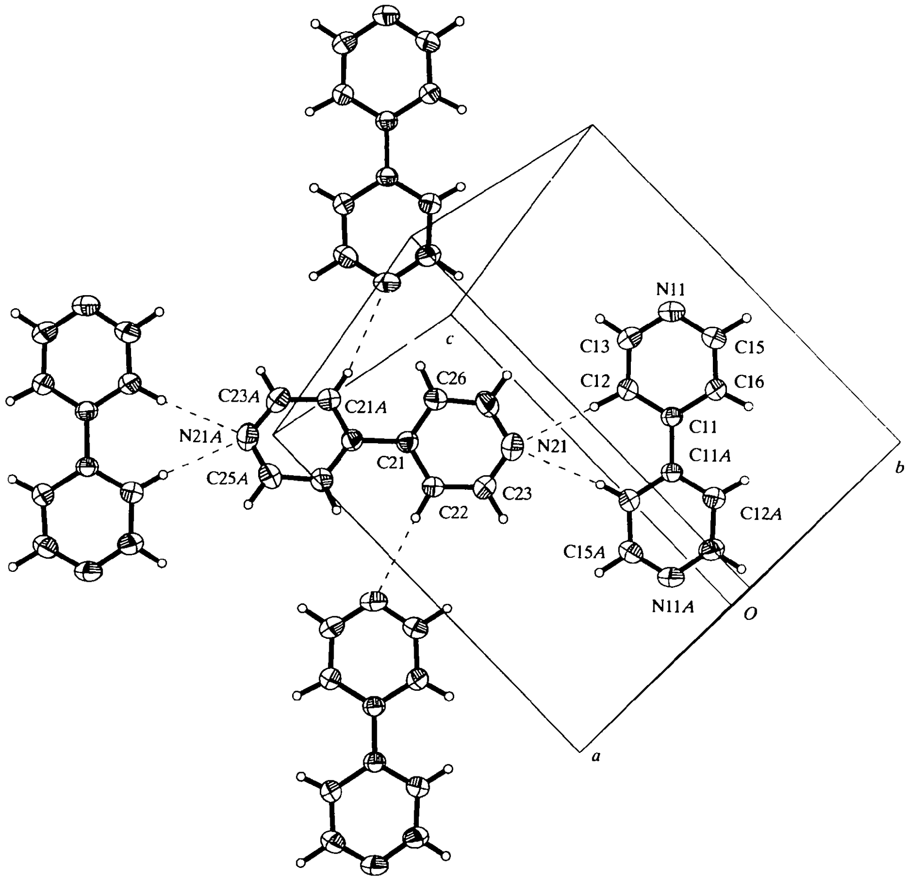


Fig. 1. The molecular structure of 4,4′-bipyridyl showing hydrogen bonding. Molecule 1 is on the right. The displacement ellipsoids are drawn at the 50% probability level.

subtended at nitrogen averages 116°. This results in an opening up of the internal angle at the adjacent carbon to some 124° and a corresponding reduction of the internal angle at the ring-connecting carbon to 117°, a ring geometry distortion paralleled in similar systems (Gourdon, 1993). The H atoms were located and fully refined.

The mean planes of the two independent molecules subtend an angle of 14.1 (8)° to each other whereas the angle subtended by the two vectors arising from projection of the inter-annular bonds of the two molecules onto a common mean plane is approximately 88°. This orientation permits bidentate hydrogen bonding between each N atom and two H atoms on the C atoms adjacent to the ring-linking C—C bond resulting in a sheet structure (Fig. 1) with a distance of approximately 4.5 Å between adjacent sheets. There are no obvious interactions between the sheets. Of the eight possible hydrogen bonds to nitrogen, six lie in the range 2.48 to 2.63 Å, clearly indicative of some form of interaction (Taylor & Kennard, 1982). The two remaining interactions at 2.74 and 2.82 Å lie close to the sum of the van der Waals radii (Mascal, 1998) and may be coincidental. The variation in the dihedral angle found in the solid and gas states is suggestive of a low rotation barrier of the two phenyl groups with respect to each other and this angle may well be influenced by the nitrogen–hydrogen interactions.

Experimental

A complex spectroscopically identified as a 2:1 adduct of triethylgallium and 4,4′-bipyridyl was dissolved in dry hexane (0.1 g in 7 ml) under dinitrogen and cooled to 243 K. After one week, crystals of 4,4′-bipyridyl were isolated from the solution and dried in a stream of dinitrogen. The crystals proved extremely friable and data were subsequently collected on the smallest crystal isolated. The length of this crystal (1.0 mm) was the same order of magnitude as the diameter of the X-ray beam, however, since a satisfactory solution was obtained, no volume correction was applied to the data.

Crystal data

$C_{10}H_8N_2$ Mo $K\alpha$ radiation
$M_r = 156.19$ $\lambda = 0.71073$ Å

Triclinic
$P\overline{1}$
$a = 8.778$ (2) Å
$b = 8.781$ (1) Å
$c = 10.998$ (2) Å
$\alpha = 85.52$ (1)°
$\beta = 85.42$ (2)°
$\gamma = 78.57$ (1)°
$V = 826.6$ (3) Å^3
$Z = 4$
$D_x = 1.255$ Mg m^{-3}
D_m not measured
Cell parameters from 32 reflections
$\theta = 4.746$–14.863°
$\mu = 0.077$ mm^{-1}
$T = 203$ (2) K
Irregular block
1.00 × 0.30 × 0.20 mm
Colourless

Data collection

Siemens *P*4 diffractometer
Profile fitting of $\theta/2\theta$ scans
Absorption correction: none
3910 measured reflections
3170 independent reflections
2031 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\rm max} = 27.49°$
$h = -11 \rightarrow 1$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.051$
$wR(F^2) = 0.134$
$S = 1.010$
3170 reflections
281 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.2120P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N11—C13	1.326 (3)	N21—C25	1.329 (3)
N11—C15	1.329 (3)	N21—C23	1.335 (3)
C11—C16	1.381 (3)	C21—C22	1.388 (3)
C11—C12	1.383 (3)	C21—C26	1.388 (3)
C11—C11*A*	1.494 (3)	C21—C21*A*	1.484 (3)
C12—C13	1.379 (3)	C22—C23	1.380 (3)
C15—C16	1.379 (3)	C25—C26	1.380 (3)
N11*A*—C15*A*	1.331 (3)	N21*A*—C25*A*	1.333 (3)
N11*A*—C13*A*	1.335 (3)	N21*A*—C23*A*	1.335 (3)
C11*A*—C12*A*	1.385 (3)	C21*A*—C26*A*	1.389 (3)
C11*A*—C16*A*	1.391 (3)	C21*A*—C22*A*	1.391 (3)
C12*A*—C13*A*	1.385 (3)	C22*A*—C23*A*	1.376 (3)
C15*A*—C16*A*	1.386 (3)	C25*A*—C26*A*	1.381 (3)
C13—N11—C15	115.45 (19)	C25—N21—C23	115.8 (2)
C16—C11—C12	116.40 (18)	C22—C21—C26	117.33 (19)
C16—C11—C11*A*	121.75 (19)	C22—C21—C21*A*	120.72 (17)
C12—C11—C11*A*	121.84 (18)	C26—C21—C21*A*	121.94 (18)
C13—C12—C11	119.5 (2)	C23—C22—C21	119.2 (2)
N11—C13—C12	124.6 (2)	N21—C23—C22	124.2 (2)
N11—C15—C16	124.3 (2)	N21—C25—C26	124.8 (2)
C15—C16—C11	119.7 (2)	C25—C26—C21	118.7 (2)
C15*A*—N11*A*—C13*A*	115.82 (19)	C25*A*—N21*A*—C23*A*	116.1 (2)
C12*A*—C11*A*—C16*A*	117.08 (19)	C26*A*—C21*A*—C22*A*	117.5 (2)
C12*A*—C11*A*—C11	121.29 (19)	C26*A*—C21*A*—C21	121.00 (18)
C16*A*—C11*A*—C11	121.6 (2)	C22*A*—C21*A*—C21	121.49 (19)
C11*A*—C12*A*—C13*A*	119.4 (2)	C23*A*—C22*A*—C21*A*	119.1 (2)
N11*A*—C13*A*—C12*A*	124.2 (2)	N21*A*—C23*A*—C22*A*	124.2 (2)
N11*A*—C15*A*—C16*A*	124.5 (2)	N21*A*—C25*A*—C26*A*	124.4 (2)
C15*A*—C16*A*—C11*A*	119.0 (2)	C25*A*—C26*A*—C21*A*	118.7 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C22—H22···N11$^{\rm i}$	0.96 (2)	2.48 (2)	3.436 (3)	171.0 (19)
C26*A*—H26*A*···N11$^{\rm i}$	0.97 (2)	2.82 (2)	3.558 (3)	133.4 (17)
C26—H26···N11*A*$^{\rm ii}$	0.98 (2)	2.74 (2)	3.599 (3)	146.0 (19)
C22*A*—H22*A*···N11*A*$^{\rm ii}$	0.94 (2)	2.63 (2)	3.503 (3)	155 (2)
C12*A*—H12*A*···N21*A*$^{\rm iii}$	0.96 (2)	2.58 (2)	3.491 (3)	158.8 (18)
C16—H16···N21*A*$^{\rm iii}$	0.96 (3)	2.48 (3)	3.436 (3)	170 (2)
C16*A*—H16*A*···N21	0.91 (3)	2.61 (3)	3.514 (3)	173.3 (19)
C12—H12···N21	1.01 (2)	2.63 (3)	3.574 (3)	156.4 (19)

Symmetry codes: (i) $1 + x, y - 1, z$; (ii) $x, y, 1 + z$; (iii) $x - 1, 1 + y, z - 1$.

The crystal was mounted in a Lindemann capillary tube using Fomblin YR-1800 oil [Lancaster Synthesis, Ref. 17548 (CAS 69991-67-9)] and cooled to 203 K. The triclinic cell determined from 32 reflections could be transformed into a monoclinic *C* centred cell [$a = 10.997$ (2), $b = 11.119$ (1), $c = 13.588$ (2) Å, $\alpha = 90.01$ (1) $\beta = 95.86$ (1), $\gamma = 90.08$ (1)°]. This possibility was eliminated by axial photography. The data were collected in two shells (4.5–45 and 45–55°), combined, and Lorentz and polarization corrections applied. Difference maps showed the position of all the H atoms which were subsequently fully refined.

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*97.

The authors gratefully acknowledge the support of Epichem Ltd for a studentship (KMC).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1287). Services for accessing these data are described at the back of the journal.

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