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3,3'-Dimethyl-4,4'-bipyridine and 5,5'-Dimethyl-4,4'-bipyrimidine

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Abstract

In both title compounds, the aromatic rings adopt a staggered conformation as a result of steric repulsions. In the bipyridine derivative, the closest contacts between methyl H atoms and pyridyl H atoms are H(31)···H(172) [IUPAC pyridine C5 H atom to C3' methyl group; 2.83 (6) Å] and H(71)···H(131) [2.84 (5) Å] leading to an angle between the pyridyl least-squares planes of 81.1°. In the bipyrimidine compound, the contacts are between N(3) and methyl H(71) [2.84 (3) Å] and N(3) and methyl H(72) [2.77 (3) Å] with an angle between the pyrimidyl planes of 46.0°.

Comment

The structure determination of 3,3'-dimethyl-4,4'-bipyridine (1) and 5,5'-dimethyl-4,4'-bipyrimidine (2) was undertaken during the course of a study into the electron-transfer properties of these bridging ligands *versus* their conformational changes. Details of the syntheses will be published elsewhere (Gourdon, 1992). Crystals of (1) and (2) were obtained by vacuum sublimation at 353 and 343 K, respectively.

Although the angle between ring planes in (1) is much larger than in (2), the central C—C distance is nearly the same in both compounds [1.508 (6) Å in (1), 1.498 (4) Å in (2)], indicating single-bond character. Distortions of the ring geometries from hexagonal are comparable with those in other bipyridine compounds [from the Cambridge Structural Database (Allen, Kennard & Taylor, 1983)] and in 4,4'-bipyrimidine (Tapolsky, Robert & Launay, 1988).

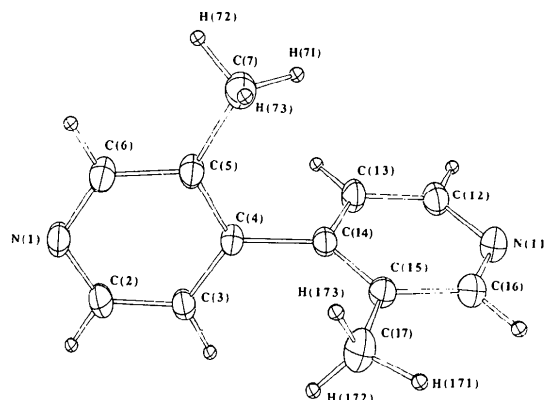


Fig. 1. View of (1) showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level except for those of H atoms which, for clarity, have an artificial U_{iso} of 0.0127 Å².

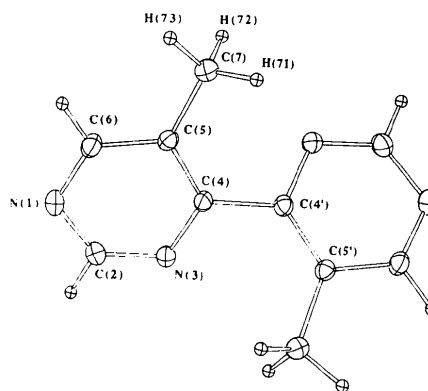


Fig. 2. View of (2) showing the atom-numbering scheme. The two halves of the molecule are related by the crystallographic two-fold axis. Thermal ellipsoids are drawn at the 30% probability level except for those of H atoms which, for clarity, have an artificial U_{iso} of 0.0127 Å².

Experimental

Compound (1)

Crystal data

$C_{12}H_{12}N_2$
 $M_r = 184.24$

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å

Monoclinic

$P2_1$
 $a = 7.492$ (3) Å
 $b = 7.505$ (5) Å
 $c = 9.502$ (3) Å
 $\beta = 109.02$ (3)°
 $V = 505.1$ (5) Å³
 $Z = 2$
 $D_x = 1.21$ Mg m⁻³

Cell parameters from 25 reflections
 $\theta = 11-14^\circ$
 $\mu = 0.0682$ mm⁻¹
 $T = 300$ K
 Rectangular plates
 $0.2 \times 0.1 \times 0.1$ mm
 Colourless

402 reflections
 74 parameters
 Unit weights applied
 $(\Delta/\sigma)_{\max} = 0.01$

Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

Data collection

CAD-4 diffractometer
 $\theta-2\theta$ scans; θ -scan width
 $(1.1 + 0.34\tan\theta)^\circ$; θ -scan
 rate 1.3-6.7° min⁻¹
 Absorption correction:
 none
 1877 measured reflections
 955 independent reflections

955 observed reflections
 $[F > 2\sigma(F)]$
 $\theta_{\max} = 25^\circ$
 $h = -9 \rightarrow 9$
 $k = -9 \rightarrow 9$
 $l = 0 \rightarrow 12$
 26 standard reflections
 frequency: 60 min
 intensity variation: 3%

Refinement

Refinement on F^2
 Final $R = 0.051$
 $wR = 0.043$
 721 reflections
 146 parameters
 Unit weights applied
 $(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.23$ e Å⁻³
 $\Delta\rho_{\min} = -0.16$ e Å⁻³
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

Compound (2)

Crystal data
 $C_{10}H_{10}N_4$
 $M_r = 186.216$
 Orthorhombic
 $P2_12_12$
 $a = 7.000$ (4) Å
 $b = 16.853$ (9) Å
 $c = 3.8986$ (7) Å
 $V = 460.0$ (4) Å³
 $Z = 2$
 $D_x = 1.345$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 25 reflections
 $\theta = 11-17^\circ$
 $\mu = 0.0811$ mm⁻¹
 $T = 300$ K
 Rectangular plates
 $0.6 \times 0.6 \times 0.1$ mm
 Colourless

Data collection

CAD-4 diffractometer
 $\theta-2\theta$ scans; θ -scan width
 $(1.2 + 0.34\tan\theta)^\circ$; θ -scan
 rate 1.3-6.7° min⁻¹
 Absorption correction:
 none
 922 measured reflections
 465 independent reflections

465 observed reflections
 $[F > 2\sigma(F)]$
 $\theta_{\max} = 24^\circ$
 $h = 0 \rightarrow 8$
 $k = 0 \rightarrow 20$
 $l = -4 \rightarrow 4$
 13 standard reflections
 frequency: 60 min
 intensity variation: none

Refinement

Refinement on F^2
 Final $R = 0.026$
 $wR = 0.026$

$\Delta\rho_{\max} = 0.12$ e Å⁻³
 $\Delta\rho_{\min} = -0.08$ e Å⁻³

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

	x	y	z	U_{eq}
$U_{eq} = (U_1U_2U_3)^{1/3}$.				
Compound (1)				
N(1)	0.6516 (6)	0.354 (1)	0.4838 (5)	0.0584
C(2)	0.7310 (7)	0.366 (1)	0.6302 (6)	0.0616
C(3)	0.6300 (7)	0.378 (1)	0.7264 (5)	0.0553
C(4)	0.4334 (6)	0.387 (1)	0.6705 (5)	0.0444
C(5)	0.3485 (7)	0.377 (1)	0.5192 (5)	0.0493
C(6)	0.4656 (7)	0.361 (1)	0.4320 (5)	0.0564
C(7)	0.1397 (8)	0.387 (2)	0.4470 (7)	0.0702
N(11)	0.1238 (7)	0.469 (1)	0.9732 (6)	0.0636
C(12)	0.1599 (8)	0.603 (1)	0.8961 (7)	0.0587
C(13)	0.2609 (9)	0.582 (1)	0.7979 (6)	0.0550
C(14)	0.3219 (7)	0.411 (1)	0.7758 (5)	0.0466
C(15)	0.2852 (7)	0.271 (1)	0.8533 (6)	0.0482
C(16)	0.1816 (9)	0.308 (1)	0.9524 (7)	0.0598
C(17)	0.337 (1)	0.086 (2)	0.8350 (8)	0.0658
Compound (2)				
N(1)	0.0970 (3)	0.2031 (1)	-0.1933 (7)	0.0474
C(2)	0.2155 (4)	0.1458 (1)	-0.0928 (8)	0.0458
N(3)	0.1853 (3)	0.0678 (1)	-0.1074 (6)	0.0400
C(4)	0.0152 (3)	0.0440 (1)	-0.2309 (7)	0.0331
C(5)	-0.1224 (3)	0.0979 (1)	-0.3430 (7)	0.0335
C(6)	-0.0696 (4)	0.1773 (1)	-0.3178 (8)	0.0427
C(7)	-0.3142 (4)	0.0770 (2)	-0.4866 (8)	0.0438

Table 2. Geometric parameters (Å, °)

Compound (1)			
N(1)—C(2)	1.326 (6)	N(11)—C(12)	1.321 (8)
N(1)—C(6)	1.319 (6)	N(11)—C(16)	1.318 (8)
C(2)—C(3)	1.368 (6)	C(12)—C(13)	1.388 (7)
C(3)—C(4)	1.395 (6)	C(13)—C(14)	1.404 (9)
C(4)—C(5)	1.371 (6)	C(14)—C(15)	1.359 (7)
C(4)—C(14)	1.508 (6)	C(15)—C(16)	1.429 (7)
C(5)—C(6)	1.395 (6)	C(15)—C(17)	1.469 (9)
C(5)—C(7)	1.491 (7)		
C(6)—N(1)—C(2)	116.6 (4)	C(16)—N(11)—C(12)	118.3 (5)
C(3)—C(2)—N(1)	123.3 (4)	C(13)—C(12)—N(11)	123.0 (6)
C(4)—C(3)—C(2)	119.6 (4)	C(14)—C(13)—C(12)	118.5 (6)
C(5)—C(4)—C(3)	117.9 (4)	C(13)—C(14)—C(4)	118.9 (5)
C(14)—C(4)—C(3)	119.8 (4)	C(15)—C(14)—C(4)	121.6 (5)
C(14)—C(4)—C(5)	122.3 (4)	C(15)—C(14)—C(13)	119.4 (5)
C(6)—C(5)—C(4)	117.4 (4)	C(16)—C(15)—C(14)	117.2 (5)
C(7)—C(5)—C(4)	122.6 (4)	C(17)—C(15)—C(14)	123.8 (5)
C(7)—C(5)—C(6)	120.0 (5)	C(17)—C(15)—C(16)	119.0 (5)
C(5)—C(6)—N(1)	125.1 (5)	C(15)—C(16)—N(11)	123.5 (5)
Compound (2)			
N(1)—C(2)	1.332 (3)	C(4)—C(4')	1.498 (4)
N(1)—C(6)	1.336 (3)	C(4)—C(5)	1.394 (3)
C(2)—N(3)	1.333 (3)	C(5)—C(6)	1.392 (3)
N(3)—C(4)	1.346 (3)	C(5)—C(7)	1.496 (4)
C(6)—N(1)—C(2)	114.5 (2)	C(5)—C(4)—C(4')	123.1 (3)
N(3)—C(2)—N(1)	127.1 (2)	C(6)—C(5)—C(4)	114.9 (2)
C(4)—N(3)—C(2)	116.7 (2)	C(7)—C(5)—C(4)	125.7 (2)
C(4')—C(4)—N(3)	114.9 (2)	C(7)—C(5)—C(6)	119.4 (2)
C(5)—C(4)—N(3)	122.0 (2)	C(5)—C(6)—N(1)	124.7 (2)

Refinement was by full-matrix least-squares methods in both cases. The aromatic H atoms were placed in calculated positions after each refinement cycle (C—H 0.98 Å). The coordinates of the methyl H atoms [H(71), H(72), H(73), H(171), H(172) and

H(173) in compound (1), H(71), H(72) and H(73) in (2)] were refined with slack constraints [C—H = 1.09 (5) Å]. Data collection: CAD-4F software. Programs used to solve structures: *SHELXS86* (Sheldrick, 1986) and *SIR88* (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989). Program used to refine structures: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Drawings prepared using *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55871 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1007]

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Structure of an Overcrowded Molecule, Benzylideneanthrone, at 193 K

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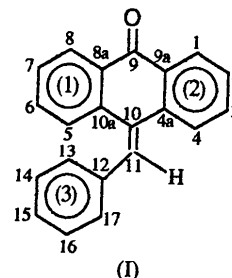
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Abstract

The central six-membered ring of the anthrone in 10-benzylidene-9(10H)-anthracenone assumes a boat conformation because of close interactions with the benzylidene moiety. Other manifestations of the overcrowding are the 6.1° twist around the double bond, the -49.5° rotation of the phenyl ring, and the increase of the C10a—C10—C11 angle to 124.1°.

Comment

In continuation of the investigation (Roberts, Anderson, Khalaf & Low, 1971; Roberts, Bantel & Low, 1973; Khalaf & Roberts, 1972; Low & Roberts, 1973; Roberts & Abdel-Baset, 1976; Prasad & Roberts, 1991) of Freidel-Crafts intramolecular cyclialkylations, the title compound (I) was prepared in order to study its reaction with acid catalysts. Synthesis was accomplished in a condensation



reaction by passing a stream of dry HCl into a stirred mixture of anthrone and benzaldehyde in a Claisen flask heated on a water bath. The product was crystallized from ethanol; the crystals were filtered, washed with a small volume of ethanol and dried. The molecule consists of an anthrone unit linked with a benzylidene moiety. All the rings are planar except the central ring (C4a, C9a, C9, C8a, C10a, C10) which has a boat conformation. The rings (1) (C5, C6, C7, C8, C8a, C10a) and (2) (C1, C2, C3, C4, C4a, C9a) are folded by 14.1 and 9.8° from the plane C4a—C9a—C8a—C10a, respectively. Ring (1) is involved in many short intramolecular contacts with ring (3) (C12, C13, C14, C15, C16, C17) (see below), and is bent downwards to a greater extent than ring (2). The dihedral angle between rings (1) and (2) is 156.2°, which is very similar to the angles found in 10-dicyanomethyleneanthrone (152°) and dianthronylideneethane (159.8 and 162.4°) (Silverman & Yannoni, 1967). Compounds exhibiting more severe overcrowding have smaller dihedral angles: α -bromo-9-(*p*-methoxybenzylidene)anthrone (139.6°) and α -tosyloxy-9-(*p*-methoxybenzylidene)anthrone (148.6°) (Kaftory, Apeloig & Rappaport, 1985); and dianthronylidene (131.9°) (Harnik & Schmidt, 1954). The double bond is twisted by 6.1°, as given by the *cis*-torsion angle, C12—C11—C10—C10a. Phenyl ring (3) is rotated around the C12—C11 bond as evidenced by the C10—C11—C12—C13 torsion angle of -49.5°. Many close interactions are observed as a result of overcrowding with atoms of the anthrone group interacting with the benzylidene group. These distances are: O···H1 = 2.475; O···H8 = 2.508; C4···H11 = 2.555; C5···C12 = 3.098; C5···C13 = 3.152; C5···H13 = 3.066; C10···H13 = 3.073; C11···H4 = 2.687; C11···H5 = 2.778; C12···H5 = 2.544; C13···C10a = 3.336; C13···H5 = 2.804; C10a···H13 = 3.024; H4···H11 = 2.069; H11···H17 = 2.597 Å. As part of the mechanism to relieve over-