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4-[4-(Methylsulfanyl)phenyl]-6-phenyl-2,2′-bipyridine

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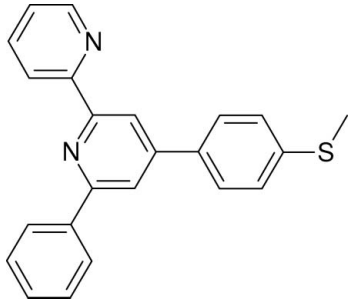
Key indicators: single-crystal X-ray study; T = 93 K; mean σ(C–C) = 0.006 Å; disorder in main residue; R factor = 0.063; wR factor = 0.161; data-to-parameter ratio = 13.2.

The structure of the title compound, $C_{23}H_{18}N_2S$, is revealed by X-ray diffraction to be almost planar over all four aromatic rings; the pendant rings are at angles of 10.18, 14.12 and 15.42° relative to the central pyridine ring for the 4-methylsulfanyl, 2-pyridyl and 6-phenyl rings, respectively. The 2,6-aromatic substituents are disordered over two sites in a 0.6:0.4 occupancy ratio.

Related literature

For related literature, see: Fitchett *et al.* (2005).



Experimental

Crystal data

$C_{23}H_{18}N_2S$
M_r = 354.45
Monoclinic, $P2_1/c$
a = 19.189 (3) Å
b = 5.3617 (8) Å
c = 17.084 (3) Å
β = 92.262 (9)°
V = 1756.3 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 93 (2) K
0.45 × 0.17 × 0.04 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.599, T_{max} = 0.992
19871 measured reflections
3118 independent reflections
1442 reflections with $I > 2\sigma(I)$
R_{int} = 0.121

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.161
S = 0.93
3118 reflections
236 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Version 1.08; Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WW2105).

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supplementary materials

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4-[4-(Methylsulfanyl)phenyl]-6-phenyl-2,2'-bipyridine

M. I. J. Polson, F. Scandola and P. J. Steel

Comment

The use of Self Assemblied Monolayers (SAMs) in the fabrication of molecular devices is a rapidly expanding field. To incorporate the useful photophysical properties of iridium complexes into a SAM, ligands must be capable of attaching to a surface. The compound (1), a bipyridine based ligand, includes a protected thiol group for attachment to a gold surface and a phenyl group for cyclometallation. Typically bipyridine ligands crystallize with the pyridine N atoms in a s-*trans* arrangement (Fitchett *et al.*, 2005). This is attributed to reduction of C—H/H—C interactions. Here, the pyridine ring and the phenyl ring crystallize in identical conformations, leading to disorder. If C—H/H—C interactions were the dominant force for the arrangement of the ring, one would expect the phenyl ring to adopt a different arrangement due to the additional interaction. This implies that the dominant force for the arrangement of the rings is the attractive C—H/N interaction.

Experimental

To a solution of 4-(methylsulfanyl)benzaldehyde (5 g), acetophenone (4.5 g), methanol (300 ml) and ammonia (0.81 g/ml, 50 ml) was added a sodium hydroxide solution (1.5 g in 50 ml water) with stirring. Overnight a precipitate of the condensation product formed. This was filtered, air dried and was used in the next step without further purification. This compound (5 g) was ground in a mortar and pestle with 2-acetylpyridine (2.5 g) and sodium hydroxide (0.83 g) until the mixture became a solid again. Excess ammonium hydroxide was added and the mixture dissolved in glacial acetic acid (50 ml) and was refluxed with stirring for 4 h. On cooling, the solution was poured into water (200 ml) and extracted with dichloromethane (3 *x* 50 ml). Chromatography on silica gel with dichloromethane/methanol (95:5) yielded the pure product (1). Single crystals suitable for X-ray diffraction formed on slow evaporation from dichloromethane solution. Yield = 2.3 g (25%). Spectroscopic data: ^{1}H NMR ($CDCl_3$): δ 2.54 (3*H*, s, CH_3S), 7.35 (1*H*, ddd, py5'), 7.37 (2*H*, d, thio-ph3,5), 7.46 (1*H*, t, ph4), 7.53 (2*H*, dd, thio-ph2,6), 7.77 (2*H*, d, ph3,5), 7.87 (1*H*, td, py4'), 7.95 (1*H*, d, py5), 8.20 (2*H*, d, ph2,6), 8.63 (1*H*, d, py3), 8.68 (1*H*, d, py3'), 8.72 (1*H*, dd, py6'); ^{13}C NMR ($CDCl_3$): δ 15.5, 117.1, 118.1, 121.6, 123.9, 126.5, 127.1, 127.5, 128.7, 129.1, 135.0, 137.1, 139.4, 140.1, 148.8, 149.5, 156.0, 156.2, 157.2.

Refinement

The 2-pyridine and 6-phenyl rings are disordered in a 60/40 ratio over the two possible positions. The pyridine ring however always adopts a s-*trans* arrangement to the central pyridine nitrogen, presumably to minimize hydrogen/hydrogen repulsions.

Figures

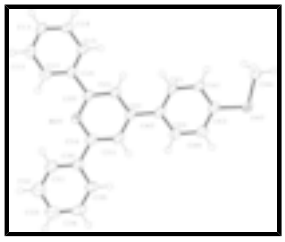


Fig. 1. The molecular structure of (1), showing displacement ellipsoids at the 50% probability level.

4-[4-(Methylsulfanyl)phenyl]-6-phenyl-2,2'-bipyridine

Crystal data

$C_{23}H_{18}N_2S$	F_{000} = 744
M_r = 354.45	D_x = 1.341 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 1819 reflections
a = 19.189 (3) Å	θ = 2.7–25.9º
b = 5.3617 (8) Å	μ = 0.19 mm^{-1}
c = 17.084 (3) Å	T = 93 (2) K
β = 92.262 (9)º	Plate, yellow
V = 1756.3 (5) Å^3	0.45 × 0.17 × 0.04 mm
Z = 4	

Data collection

Bruker APEXII CCD area-detector diffractometer	3118 independent reflections
Radiation source: sealed tube	1442 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.121
T = 93(2) K	θ_{max} = 25.1º
φ and ω scans	θ_{min} = 2.4º
Absorption correction: multi-scan (SADABS; Bruker, 2007)	h = −22→22
T_{min} = 0.599, T_{max} = 0.992	k = −6→6
19871 measured reflections	l = −20→20

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.063	H-atom parameters constrained
$wR(F^2)$ = 0.161	$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.5007P]$ where $P = (F_o^2 + 2F_c^2)/3$

S = 0.93	$(\Delta/\sigma)_{max} < 0.001$
3118 reflections	$\Delta\rho_{max}$ = 0.50 e Å^{-3}
236 parameters	$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C10	0.7765 (2)	0.5910 (7)	0.4911 (2)	0.0262 (10)	
C11	0.8384 (2)	0.6255 (8)	0.5330 (3)	0.0467 (13)	
H11	0.8788	0.5333	0.5204	0.056*	
C12	0.8411 (2)	0.7978 (9)	0.5941 (3)	0.0575 (15)	
H12	0.8832	0.8205	0.6245	0.069*	
C13	0.7843 (2)	0.9318 (8)	0.6101 (2)	0.0383 (11)	
H13	0.7862	1.0516	0.6511	0.046*	
C14	0.7242 (2)	0.8947 (9)	0.5672 (3)	0.0440 (12)	
H14	0.6839	0.9883	0.5792	0.053*	
N15	0.71985 (18)	0.7258 (8)	0.5069 (2)	0.0428 (10)	0.60
C15	0.71985 (18)	0.7258 (8)	0.5069 (2)	0.0428 (10)	0.40
H15	0.6775	0.7046	0.4769	0.051*	0.40
N20	0.82507 (15)	0.2544 (7)	0.41731 (17)	0.0296 (8)	
C20	0.7730 (2)	0.4149 (8)	0.4222 (2)	0.0278 (10)	
C21	0.7176 (2)	0.4300 (8)	0.3674 (2)	0.0300 (10)	
H21	0.6811	0.5471	0.3741	0.036*	
C22	0.71595 (19)	0.2711 (8)	0.3022 (2)	0.0269 (9)	
C23	0.7708 (2)	0.1064 (8)	0.2974 (2)	0.0322 (11)	
H23	0.7720	−0.0040	0.2540	0.039*	
C24	0.8246 (2)	0.0983 (8)	0.3549 (2)	0.0314 (10)	
C30	0.8832 (2)	−0.0776 (8)	0.3508 (2)	0.0306 (10)	
C31	0.9434 (2)	−0.0504 (9)	0.3971 (3)	0.0453 (13)	
H31	0.9469	0.0856	0.4327	0.054*	
C32	0.9981 (3)	−0.2125 (10)	0.3934 (3)	0.0545 (14)	
H32	1.0387	−0.1896	0.4262	0.065*	
C33	0.9939 (2)	−0.4123 (9)	0.3407 (3)	0.0454 (13)	
H33	1.0314	−0.5261	0.3361	0.054*	

C34	0.9338 (2)	−0.4371 (9)	0.2964 (3)	0.0441 (12)	
H34	0.9297	−0.5751	0.2617	0.053*	
N35	0.87914 (19)	−0.2752 (8)	0.2989 (2)	0.0354 (10)	0.40
C35	0.87914 (19)	−0.2752 (8)	0.2989 (2)	0.0354 (10)	0.60
H35	0.8389	−0.2979	0.2655	0.042*	0.60
C40	0.65707 (19)	0.2792 (8)	0.2432 (2)	0.0283 (10)	
C41	0.6070 (2)	0.4625 (8)	0.2429 (2)	0.0380 (11)	
H41	0.6118	0.5930	0.2803	0.046*	
C42	0.5494 (2)	0.4669 (8)	0.1906 (2)	0.0393 (12)	
H42	0.5163	0.5981	0.1928	0.047*	
C43	0.54081 (19)	0.2767 (8)	0.1349 (2)	0.0302 (10)	
C44	0.5919 (2)	0.0955 (9)	0.1327 (3)	0.0442 (12)	
H44	0.5880	−0.0321	0.0943	0.053*	
C45	0.6486 (2)	0.0961 (8)	0.1857 (3)	0.0411 (12)	
H45	0.6827	−0.0318	0.1826	0.049*	
S40	0.46881 (5)	0.2541 (2)	0.06834 (6)	0.0347 (3)	
C46	0.4188 (2)	0.5257 (8)	0.0889 (2)	0.0422 (12)	
H46A	0.4083	0.5279	0.1446	0.063*	
H46B	0.3752	0.5232	0.0571	0.063*	
H46C	0.4456	0.6752	0.0763	0.063*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C10	0.032 (2)	0.030 (2)	0.016 (2)	−0.001 (2)	0.0034 (18)	0.005 (2)
C11	0.048 (3)	0.050 (3)	0.041 (3)	0.015 (2)	−0.006 (2)	−0.015 (3)
C12	0.056 (3)	0.071 (4)	0.044 (3)	0.019 (3)	−0.024 (2)	−0.021 (3)
C13	0.052 (3)	0.043 (3)	0.019 (3)	0.003 (2)	−0.004 (2)	−0.007 (2)
C14	0.046 (3)	0.050 (3)	0.037 (3)	0.014 (2)	0.004 (2)	−0.019 (3)
N15	0.043 (2)	0.058 (3)	0.028 (2)	0.007 (2)	−0.0014 (17)	−0.019 (2)
C15	0.043 (2)	0.058 (3)	0.028 (2)	0.007 (2)	−0.0014 (17)	−0.019 (2)
N20	0.0384 (19)	0.037 (2)	0.0137 (18)	0.003 (2)	0.0057 (14)	0.0044 (19)
C20	0.037 (2)	0.034 (3)	0.012 (2)	0.001 (2)	0.0076 (19)	0.002 (2)
C21	0.042 (3)	0.029 (3)	0.019 (2)	0.000 (2)	0.002 (2)	0.001 (2)
C22	0.039 (2)	0.029 (2)	0.013 (2)	−0.002 (2)	0.0067 (17)	0.004 (2)
C23	0.048 (3)	0.036 (3)	0.013 (2)	−0.002 (2)	0.003 (2)	−0.001 (2)
C24	0.043 (3)	0.029 (3)	0.022 (3)	−0.002 (2)	0.006 (2)	0.005 (2)
C30	0.039 (3)	0.037 (3)	0.016 (2)	0.003 (2)	0.0086 (19)	0.006 (2)
C31	0.056 (3)	0.056 (3)	0.024 (3)	0.013 (3)	0.001 (2)	−0.003 (2)
C32	0.064 (3)	0.071 (4)	0.029 (3)	0.018 (3)	0.000 (2)	0.007 (3)
C33	0.056 (3)	0.046 (3)	0.035 (3)	0.012 (3)	0.011 (2)	0.013 (3)
C34	0.062 (3)	0.040 (3)	0.032 (3)	0.003 (3)	0.018 (3)	−0.003 (2)
N35	0.048 (2)	0.036 (2)	0.023 (2)	0.006 (2)	0.0093 (18)	0.000 (2)
C35	0.048 (2)	0.036 (2)	0.023 (2)	0.006 (2)	0.0093 (18)	0.000 (2)
C40	0.039 (2)	0.031 (3)	0.016 (2)	−0.005 (2)	0.0059 (17)	0.003 (2)
C41	0.053 (3)	0.045 (3)	0.016 (3)	0.005 (2)	−0.002 (2)	−0.010 (2)
C42	0.055 (3)	0.041 (3)	0.022 (3)	0.012 (2)	0.001 (2)	−0.007 (2)
C43	0.038 (2)	0.029 (3)	0.024 (2)	−0.005 (2)	0.0013 (18)	0.004 (2)

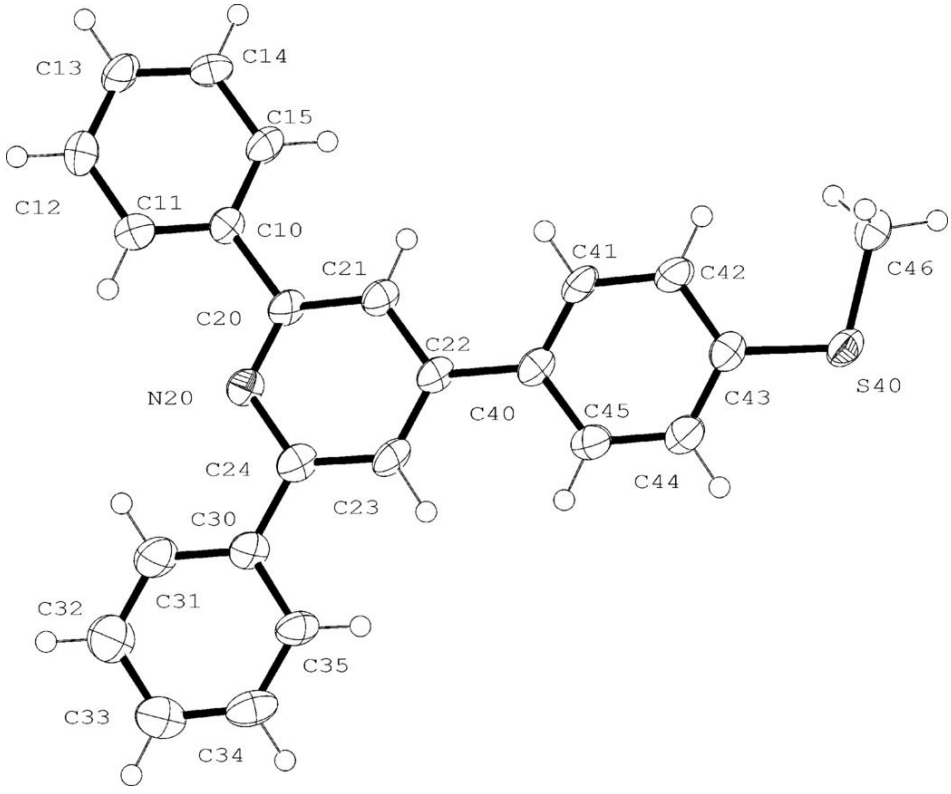
C44	0.056 (3)	0.040 (3)	0.036 (3)	0.006 (3)	−0.008 (2)	−0.011 (2)
C45	0.052 (3)	0.034 (3)	0.037 (3)	0.010 (2)	−0.004 (2)	−0.009 (2)
S40	0.0459 (6)	0.0359 (6)	0.0222 (6)	−0.0007 (6)	−0.0005 (4)	−0.0047 (6)
C46	0.049 (3)	0.053 (3)	0.024 (3)	0.009 (2)	−0.003 (2)	−0.003 (2)

Geometric parameters (Å, °)

C10—N15	1.342 (5)	C31—C32	1.367 (6)
C10—C11	1.374 (5)	C31—H31	0.9500
C10—C20	1.509 (5)	C32—C33	1.399 (6)
C11—C12	1.394 (6)	C32—H32	0.9500
C11—H11	0.9500	C33—C34	1.360 (6)
C12—C13	1.343 (6)	C33—H33	0.9500
C12—H12	0.9500	C34—N35	1.364 (5)
C13—C14	1.357 (5)	C34—H34	0.9500
C13—H13	0.9500	C40—C41	1.375 (5)
C14—N15	1.371 (5)	C40—C45	1.393 (5)
C14—H14	0.9500	C41—C42	1.392 (5)
N20—C20	1.324 (5)	C41—H41	0.9500
N20—C24	1.355 (5)	C42—C43	1.401 (6)
C20—C21	1.391 (5)	C42—H42	0.9500
C21—C22	1.402 (5)	C43—C44	1.381 (6)
C21—H21	0.9500	C43—S40	1.758 (4)
C22—C23	1.378 (5)	C44—C45	1.388 (6)
C22—C40	1.485 (5)	C44—H44	0.9500
C23—C24	1.398 (5)	C45—H45	0.9500
C23—H23	0.9500	S40—C46	1.787 (4)
C24—C30	1.472 (5)	C46—H46A	0.9800
C30—C31	1.380 (6)	C46—H46B	0.9800
C30—N35	1.382 (5)	C46—H46C	0.9800
N15—C10—C11	120.9 (4)	C30—C31—H31	118.9
N15—C10—C20	118.8 (4)	C31—C32—C33	119.5 (5)
C11—C10—C20	120.1 (4)	C31—C32—H32	120.3
C10—C11—C12	119.0 (4)	C33—C32—H32	120.3
C10—C11—H11	120.5	C34—C33—C32	117.3 (5)
C12—C11—H11	120.5	C34—C33—H33	121.3
C13—C12—C11	120.1 (4)	C32—C33—H33	121.3
C13—C12—H12	120.0	C33—C34—N35	123.8 (5)
C11—C12—H12	120.0	C33—C34—H34	118.1
C12—C13—C14	119.4 (4)	N35—C34—H34	118.1
C12—C13—H13	120.3	C34—N35—C30	118.9 (4)
C14—C13—H13	120.3	C41—C40—C45	116.1 (4)
C13—C14—N15	121.8 (4)	C41—C40—C22	122.4 (4)
C13—C14—H14	119.1	C45—C40—C22	121.5 (4)
N15—C14—H14	119.1	C40—C41—C42	123.4 (4)
C10—N15—C14	118.8 (4)	C40—C41—H41	118.3
C20—N20—C24	117.9 (3)	C42—C41—H41	118.3
N20—C20—C21	123.7 (4)	C41—C42—C43	119.5 (4)
N20—C20—C10	116.4 (3)	C41—C42—H42	120.2

C21—C20—C10	119.9 (4)	C43—C42—H42	120.2
C20—C21—C22	119.4 (4)	C44—C43—C42	117.7 (4)
C20—C21—H21	120.3	C44—C43—S40	118.3 (3)
C22—C21—H21	120.3	C42—C43—S40	123.9 (3)
C23—C22—C21	116.4 (3)	C43—C44—C45	121.4 (4)
C23—C22—C40	122.7 (4)	C43—C44—H44	119.3
C21—C22—C40	120.9 (4)	C45—C44—H44	119.3
C22—C23—C24	121.5 (4)	C44—C45—C40	121.8 (4)
C22—C23—H23	119.3	C44—C45—H45	119.1
C24—C23—H23	119.3	C40—C45—H45	119.1
N20—C24—C23	121.1 (4)	C43—S40—C46	103.4 (2)
N20—C24—C30	116.8 (4)	S40—C46—H46A	109.5
C23—C24—C30	122.1 (4)	S40—C46—H46B	109.5
C31—C30—N35	118.2 (4)	H46A—C46—H46B	109.5
C31—C30—C24	121.9 (4)	S40—C46—H46C	109.5
N35—C30—C24	119.8 (4)	H46A—C46—H46C	109.5
C32—C31—C30	122.2 (5)	H46B—C46—H46C	109.5
C32—C31—H31	118.9		

Fig. 1


C13
C14
C15
C12
C11
C10
C21
C20
C22
N20
C40
C24
C23
C30
C31
C32
C35
C33
C34
C41
C42
C46
C45
C43
S40
C44