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1-Methyl-3-(5-methylthiazol-2-yldiazenyl)-2-phenyl-1*H*-indole

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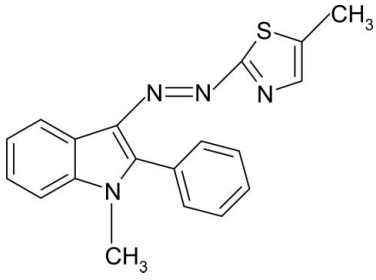
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.003 Å; R factor = 0.052; wR factor = 0.173; data-to-parameter ratio = 17.8.

In the title compound, $C_{19}H_{16}N_4S$, the thiazole and phenyl rings form dihedral angles of 13.97 (4) and 47.79 (6)°, respectively, with the indole ring system.

Related literature

For general background, see: Zabriskie *et al.* (1988); Metzger (1984); Kornis (1984); Comba (1993); Chohan *et al.* (2002); Florin *et al.* (1980); Rau (1990); Bach *et al.* (1996); Biswas & Umapathy (2000); Ochiai *et al.* (1986); Tsuda *et al.* (2000); Allen *et al.* (1987). For related literature, see: Bruni *et al.* (1995); Seferoğlu *et al.* (2006*a*,*b*,*c*, 2007*a*,*b*,*c*; Seferoğlu, Hökelek, Şahin *et al.* (2006); Hökelek *et al.* (2007).



Experimental

Crystal data

$C_{19}H_{16}N_4S$
M_r = 332.42
Triclinic, $P\overline{1}$
a = 9.2514 (7) Å
b = 9.2745 (5) Å
c = 11.0971 (6) Å
α = 106.259 (1)°
β = 106.542 (2)°
γ = 103.337 (2)°
V = 824.90 (9) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.20 mm^{-1}
T = 294 (2) K
0.35 × 0.20 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID-S diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.932, T_{max} = 0.970
24972 measured reflections
5029 independent reflections
3726 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.173
S = 1.06
5029 reflections
282 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YM2060).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bach, H., Anderle, K., Fuhrmann, Th. & Wendorff, J. H. (1996). *J. Phys. Chem.* **100**, 4135–4140.
Biswas, N. & Umapathy, S. (2000). *J. Phys. Chem. A*, **104**, 2734–2745.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruni, P., Bocelli, G., Cantoni, A., Giorgini, E., Iacussi, M., Maurelli, E. & Tosi, G. (1995). *J. Chem. Crystallogr.* **25**, 683–691.
Chohan, Z. H., Pervez, H., Rauf, A., Scozzafava, A. & Supuran, C. T. (2002). *J. Enzyme Inhib. Med. Chem.* **17**, 117–122.
Comba, P. (1993). *Coord. Chem. Rev.* **123**, 1–48.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Florin, I., Rutburge, L., Curvall, M. & Enzell, C. R. (1980). *Toxicology*, **18**, 219–232.
Hökelek, T., Seferoğlu, Z., Şahin, E. & Kaynak, F. B. (2007). *Acta Cryst.* E**63**, o2837–o2839.
Kornis, G. (1984). *1,3,4-Thiadizoles in Comphrensive Heterocyclic Chemistry*, edited by A. R. Katritzky, Vol. 6, Part 4B, pp. 545–578. New York: Pergamon Press.
Metzger, J. V. (1984). *Thiazoles and their Benzo Derivatives*, edited by K. T. Potts, Vol. 6. New York: Pergamon Press.
Ochiai, M., Wakabayashi, K., Sugimura, T. & Nagao, M. (1986). *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* **172**, 189–197.
Rau, H. (1990). *Photochromism. Molecules and Systems*, edited by H. Dürr & H. Bouas-Laurent, ch. 4, p. 165. Amsterdam: Elsevier.
Rigaku/MSC (2005). *CrystalClear*. Rigaku/MSC, The Woodlands, Texas, USA.
Seferoğlu, Z., Hökelek, T., Şahin, E. & Ertan, N. (2006*a*). *Acta Cryst.* E**62**, o2108–o2110.
Seferoğlu, Z., Hökelek, T., Şahin, E. & Ertan, N. (2006*b*). *Acta Cryst.* E**62**, o3492–o3494.
Seferoğlu, Z., Hökelek, T., Şahin, E. & Ertan, N. (2006*c*). *Acta Cryst.* E**62**, o3835–o3837.
Seferoğlu, Z., Hökelek, T., Şahin, E. & Ertan, N. (2007*a*). *Acta Cryst.* E**63**, o148–o150.
Seferoğlu, Z., Hökelek, T., Şahin, E. & Ertan, N. (2007*b*). *Acta Cryst.* E**63**, o351–o353.

Seferoğlu, Z., Hökelek, T., Şahin, E. & Ertan, N. (2007*c*). *Acta Cryst.* E**63**, o568–o570.
Seferoğlu, Z., Hökelek, T., Şahin, E., Saylam, A. & Ertan, N. (2006). *Acta Cryst.* E**62**, o5488–o5489.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Tsuda, S., Matsusaka, N., Madarame, H., Ueno, S., Susa, N., Ishida, K., Kawamura, N., Sekihashi, K. & Sasaki, Y. F. (2000). *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* **465**, 11–26.
Zabriskie, T. M., Mayne, C. L. & Ireland, C. M. (1988). *J. Am. Chem. Soc.* **110**, 7919–7920.

supplementary materials

Acta Cryst. (2007). E**63**, o3281-o3282 [**doi:10.1107/S1600536807029571**]

1-Methyl-3-(5-methylthiazol-2-yldiazenyl)-2-phenyl-1*H*-indole

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Comment

Heterocycles containing the 1,3-thiazole ring system exhibit a wide spectrum of biological activities, including acting as antiviral and antifungal agents, and that ring has been identified as a central structural element of a number of biologically active natural products (Zabriskie *et al.*, 1988) and of pharmacologically active compounds (Metzger, 1984). The bioactivity of *S*,*N*-thiazoles is mainly due to their structural similarities with proteins' imidazolyl entities (Kornis, 1984) as well as their biological, structural, electronic and spectroscopic properties (Comba, 1993). Their existence may modify the bioactive and pharmaceutical characteristics of the adducts (Chohan *et al.*, 2002).

Indole and its derivatives form a class of toxic recalcitrant N-heterocyclic compounds that are considered as pollutants (Florin *et al.*, 1980). Azo derivatives are used extensively in analytical chemistry and in dyestuff industry as metallochromic and acid-base indicators (Rau, 1990). They are also used in the fields of non-linear optics and optical data storage (Bach *et al.*, 1996). Azo dyes have wide applicability as optical materials and their structures have also attracted considerable attention (Biswas & Umapathy, 2000). Many azo-dye breakdown products are carcinogenic, toxic or mutagenic to life (Ochiai *et al.*, 1986). Although there are many publications on the industrial applications of azo dyes (Tsuda *et al.*, 2000), to the best of our knowledge, few structures of azoindole derivatives have been reported to date (Bruni *et al.*, 1995; Seferoğlu *et al.*, 2006*a*,b,c; Seferoğlu *et al.*, 2006; Seferoğlu *et al.*, 2007*a*,b,c; Hökelek *et al.*, 2007). The present study was undertaken in order to ascertain the crystal structure of the title compound, (I).

The molecular structure of (I), is shown in Fig. 1. The bond lengths and angles are in normal ranges (Allen *et al.*, 1987).

An examination of the deviations from the least-squares planes through the individual rings shows that all the rings are planar. The indole ring system is planar, with a dihedral angle of 0.72 (6)° between rings A (C5—C10) and B (N4/C4/C5/C10/C11). In the closely related compounds 3-(4-chlorophenyldiazenyl)-1-methyl-2-phenyl-1*H*-indole, (II) (Seferoğlu *et al.*, 2006*a*), *N*-{4-[(2-phenyl-1*H*-indol-3-yl)diazenyl]phenyl}acetamide, (III) (Seferoğlu *et al.*, 2006*b*), ethyl[2-(2-phenyl-1*H*-indol-3-yldiazenyl)-1,3 -thiazol-4-yl]acetate, (IV) (Seferoğlu *et al.*, 2006*c*), ethyl-2-{2-[(1-methyl-2-phenyl-1*H*-indol-3-yl)diazenyl]thiazol-4-yl}acetate, (V) (Seferoğlu *et al.*, 2006), 1-methyl-2-phenyl-3-(1,3,4-thiadiazol-2-yldiazenyl)-1*H*-indole, (VI) (Seferoğlu *et al.*, 2007*a*), 1,2-dimethyl-3-(thiazol-2-yldazenyl)-1*H*-indole, (VII) (Seferoğlu *et al.*, 2007*b*), 3-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)-1-Methyl-2-phenyl-1*H*-indole, (VIII) (Seferoğlu *et al.*, 2007*c*) and 3-(6-methoxybenzothiazol-2-yldiazenyl)-1-methyl −2-phenyl-1*H*-indole, (IX) (Hökelek *et al.*, 2007), the observed A/B and/or A'/B' dihedral angles are 1.56 (11) and 0.77 (12)° in (II), 1.63 (14)° in (III), 0.99 (10)° in (IV) and 0.59 (7)° in (V), 4.26 (7)° in (VI), 2.07 (9) and 2.04 (9)° in (VII), 0.59 (12)° in (VIII) and 1.16 (7)° in (IX). The orientations of rings C (S1/N1/C1—C3) and D (C12—C17) with respect to the indole ring system may be described by the dihedral angles of 13.97 (4) and 47.79 (6)°, respectively.

As can be seen from the packing diagram (Fig. 2), the molecules of (I) are stacked along the *a* axis and elongated along the *b* axis. Dipole-dipole and van der Waals interactions are effective in the molecular packing.

Experimental

For the preparation of the title compound, 2-amino-5-methylthiazole (230 mg, 2 mmol) was dissolved in a hot glacial acetic acid-propionic acid mixture (2:1, 8 ml). The solution was rapidly cooled in an ice-salt bath and then added dropwise with stirring to a cold solution of nitrosylsulfuric acid (3 ml) over a period of 30 min. The mixture was stirred for an additional 2 h at 273 K. The resulting diazonium salt was cooled in an ice-salt bath and then added dropwise with stirring to 1-methyl-2-phenylindole (414 mg, 2 mmol) in an acetic acid-propionic acid mixture (3:1, 8 ml). The solution was stirred at 273–278 K for 2 h and the pH of the reaction mixture was maintained at 4–6 by the addition of a saturated sodium carbonate solution (40 ml). The mixture was stirred for a further 1 h. The resulting solid was filtered, washed with cold water and crystallized from ethanol (yield; 550 mg, 84%, 495–497 K).

Refinement

H atoms were located in difference syntheses and refined isotropically [C—H = 0.89 (3)–1.04 (3) Å and U_{iso}(H) = 0.062 (6)–0.110 (10) Å^2].

Figures

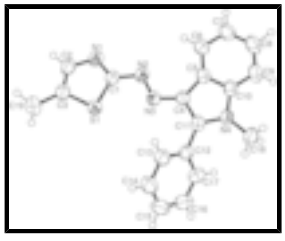

Fig. 1. A drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

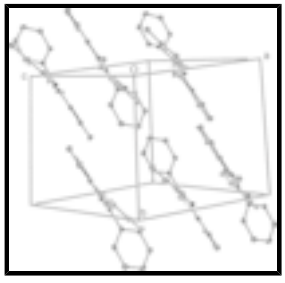

Fig. 2. A packing diagram of (I). H atoms have been omitted.

1-Methyl-3-(5-methylthiazol-2-yldiazenyl)-2-phenyl-1*H*-indole

Crystal data

$C_{19}H_{16}N_4S$	$Z = 2$
$M_r = 332.42$	$F_{000} = 348$
Triclinic, $P\bar{1}$	$D_x = 1.338$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 9.2514$ (7) Å	Cell parameters from 5548 reflections
$b = 9.2745$ (5) Å	$\theta = 2.1$–30.6º

c = 11.0971 (6) Å	μ = 0.20 mm^{-1}
α = 106.2590 (10)º	T = 294 (2) K
β = 106.542 (2)º	Rod-shaped, red
γ = 103.337 (2)º	0.35 × 0.20 × 0.15 mm
V = 824.90 (9) Å^3	

Data collection

Rigaku R-AXIS RAPID-S diffractometer	5029 independent reflections
Radiation source: fine-focus sealed tube	3726 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.058
T = 294(2) K	θ_{max} = 30.6º
ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (Blessing, 1995)	h = −11→13
T_{min} = 0.932, T_{max} = 0.970	k = −13→13
24972 measured reflections	l = −15→15

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)]$ = 0.052	$w = 1/[\sigma^2(F_o^2) + (0.0946P)^2 + 0.0434P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.173	$(\Delta/\sigma)_{max} < 0.001$
S = 1.06	$\Delta\rho_{max}$ = 0.32 e Å^{-3}
5029 reflections	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
282 parameters	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.062 (8)
Secondary atom site location: difference Fourier map	

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}
S1	0.48122 (5)	0.83549 (5)	0.31455 (4)	0.05207 (17)
N1	0.57518 (19)	1.0153 (2)	0.19243 (15)	0.0583 (4)
N2	0.76648 (16)	1.08163 (17)	0.41078 (14)	0.0493 (3)
N3	0.79155 (15)	1.01851 (16)	0.50037 (13)	0.0453 (3)
N4	1.10746 (17)	1.14326 (17)	0.81588 (13)	0.0493 (3)
C1	0.6195 (2)	0.98952 (19)	0.30474 (17)	0.0475 (4)
C2	0.4254 (2)	0.9083 (2)	0.10821 (19)	0.0590 (4)
C3	0.3545 (2)	0.8044 (2)	0.15525 (18)	0.0532 (4)
C4	0.92786 (19)	1.10103 (19)	0.61325 (16)	0.0450 (3)
C5	1.05265 (19)	1.25219 (19)	0.65531 (16)	0.0457 (3)
C6	1.0817 (2)	1.3684 (2)	0.5996 (2)	0.0543 (4)
C7	1.2172 (2)	1.5033 (2)	0.6738 (2)	0.0648 (5)
C8	1.3228 (3)	1.5235 (3)	0.8000 (2)	0.0686 (5)
C9	1.2963 (2)	1.4093 (3)	0.8561 (2)	0.0629 (5)
C10	1.16079 (19)	1.2736 (2)	0.78208 (17)	0.0476 (4)
C11	0.96765 (19)	1.0384 (2)	0.71412 (16)	0.0456 (3)
C12	0.8817 (2)	0.8837 (2)	0.71330 (16)	0.0475 (4)
C13	0.7158 (2)	0.8344 (2)	0.67463 (19)	0.0557 (4)
C14	0.6323 (3)	0.6842 (3)	0.6636 (2)	0.0708 (6)
C15	0.7136 (3)	0.5829 (3)	0.6911 (2)	0.0767 (6)
C16	0.8769 (3)	0.6300 (3)	0.7305 (2)	0.0674 (5)
C17	0.9622 (3)	0.7798 (2)	0.74165 (19)	0.0575 (4)
C18	1.1814 (3)	1.1384 (3)	0.9485 (2)	0.0619 (5)
C19	0.1894 (3)	0.6815 (3)	0.0887 (3)	0.0685 (5)
H2	0.375 (3)	0.910 (3)	0.019 (2)	0.077 (7)*
H6	1.009 (3)	1.358 (3)	0.515 (2)	0.075 (7)*
H7	1.238 (3)	1.586 (3)	0.637 (3)	0.084 (7)*
H8	1.418 (4)	1.629 (4)	0.853 (3)	0.108 (9)*
H9	1.365 (3)	1.424 (3)	0.940 (2)	0.065 (6)*
H13	0.662 (3)	0.902 (2)	0.658 (2)	0.062 (6)*
H14	0.526 (3)	0.651 (3)	0.634 (3)	0.086 (8)*
H15	0.662 (4)	0.485 (4)	0.686 (3)	0.101 (9)*
H16	0.932 (3)	0.561 (3)	0.747 (3)	0.091 (8)*
H17	1.085 (3)	0.813 (3)	0.773 (2)	0.074 (6)*
H181	1.118 (4)	1.059 (4)	0.962 (3)	0.100 (9)*
H182	1.192 (3)	1.232 (4)	1.017 (3)	0.096 (8)*
H183	1.276 (4)	1.116 (3)	0.953 (3)	0.100 (9)*
H191	0.125 (4)	0.688 (3)	0.001 (3)	0.108 (9)*
H192	0.128 (4)	0.698 (3)	0.140 (3)	0.100 (9)*
H193	0.190 (4)	0.578 (4)	0.068 (3)	0.110 (10)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

S1	0.0495 (3)	0.0518 (3)	0.0478 (2)	0.00908 (18)	0.01069 (18)	0.02237 (19)
N1	0.0554 (8)	0.0677 (9)	0.0510 (8)	0.0151 (7)	0.0142 (7)	0.0311 (7)
N2	0.0450 (7)	0.0531 (8)	0.0468 (7)	0.0119 (6)	0.0126 (6)	0.0227 (6)
N3	0.0424 (7)	0.0468 (7)	0.0430 (7)	0.0133 (6)	0.0128 (5)	0.0163 (5)
N4	0.0436 (7)	0.0558 (8)	0.0403 (7)	0.0129 (6)	0.0092 (5)	0.0159 (6)
C1	0.0452 (8)	0.0503 (8)	0.0461 (8)	0.0145 (7)	0.0132 (7)	0.0215 (7)
C2	0.0541 (10)	0.0712 (12)	0.0465 (9)	0.0185 (9)	0.0087 (8)	0.0266 (8)
C3	0.0459 (9)	0.0564 (9)	0.0488 (9)	0.0152 (7)	0.0103 (7)	0.0165 (7)
C4	0.0416 (8)	0.0460 (8)	0.0428 (8)	0.0119 (6)	0.0128 (6)	0.0151 (6)
C5	0.0407 (8)	0.0473 (8)	0.0445 (8)	0.0118 (6)	0.0144 (6)	0.0142 (6)
C6	0.0510 (9)	0.0526 (9)	0.0574 (10)	0.0134 (7)	0.0193 (8)	0.0221 (8)
C7	0.0569 (11)	0.0582 (11)	0.0746 (13)	0.0075 (9)	0.0262 (10)	0.0258 (10)
C8	0.0523 (11)	0.0608 (11)	0.0710 (13)	−0.0014 (9)	0.0177 (10)	0.0151 (10)
C9	0.0458 (10)	0.0660 (11)	0.0548 (10)	0.0032 (8)	0.0103 (8)	0.0118 (9)
C10	0.0388 (8)	0.0518 (8)	0.0457 (8)	0.0108 (7)	0.0139 (6)	0.0144 (7)
C11	0.0420 (8)	0.0499 (8)	0.0420 (7)	0.0145 (6)	0.0138 (6)	0.0157 (6)
C12	0.0498 (9)	0.0519 (8)	0.0411 (7)	0.0159 (7)	0.0172 (7)	0.0182 (6)
C13	0.0505 (9)	0.0583 (10)	0.0568 (10)	0.0130 (8)	0.0194 (8)	0.0240 (8)
C14	0.0588 (12)	0.0717 (13)	0.0704 (13)	0.0028 (10)	0.0203 (10)	0.0293 (11)
C15	0.0989 (17)	0.0528 (11)	0.0704 (13)	0.0077 (11)	0.0295 (12)	0.0279 (10)
C16	0.0893 (16)	0.0596 (11)	0.0649 (12)	0.0292 (11)	0.0328 (11)	0.0324 (10)
C17	0.0655 (11)	0.0630 (10)	0.0547 (10)	0.0270 (9)	0.0260 (9)	0.0292 (8)
C18	0.0565 (11)	0.0760 (13)	0.0433 (9)	0.0171 (10)	0.0090 (8)	0.0220 (9)
C19	0.0500 (11)	0.0691 (13)	0.0620 (12)	0.0072 (9)	0.0079 (9)	0.0129 (10)

Geometric parameters (Å, °)

S1—C1	1.7355 (17)	C10—C9	1.392 (2)
S1—C3	1.7209 (18)	C11—N4	1.366 (2)
N1—C2	1.374 (2)	C11—C4	1.398 (2)
N2—C1	1.398 (2)	C11—C12	1.467 (2)
N3—N2	1.2815 (18)	C12—C13	1.393 (3)
N3—C4	1.365 (2)	C12—C17	1.396 (2)
N4—C10	1.389 (2)	C13—C14	1.381 (3)
N4—C18	1.454 (2)	C13—H13	0.91 (2)
C1—N1	1.304 (2)	C14—C15	1.378 (4)
C2—H2	0.97 (2)	C14—H14	0.89 (3)
C3—C2	1.348 (3)	C15—H15	0.90 (3)
C3—C19	1.503 (3)	C16—C15	1.370 (4)
C5—C4	1.448 (2)	C16—H16	0.93 (3)
C5—C6	1.397 (2)	C17—C16	1.383 (3)
C5—C10	1.404 (2)	C17—H17	1.03 (2)
C6—C7	1.388 (3)	C18—H181	0.91 (3)
C6—H6	0.95 (2)	C18—H182	0.94 (3)
C7—H7	0.97 (2)	C18—H183	0.94 (3)
C8—C7	1.393 (3)	C19—H191	1.01 (3)
C8—C9	1.381 (3)	C19—H192	0.92 (3)
C8—H8	1.04 (3)	C19—H193	0.92 (3)
C9—H9	0.91 (2)		

C3—S1—C1	88.89 (8)	N4—C10—C5	109.22 (14)
C1—N1—C2	109.34 (15)	C9—C10—C5	121.98 (17)
N3—N2—C1	110.10 (13)	N4—C11—C4	108.74 (15)
N2—N3—C4	116.17 (14)	N4—C11—C12	123.71 (14)
C10—N4—C18	122.69 (16)	C4—C11—C12	127.50 (15)
C11—N4—C10	109.02 (13)	C13—C12—C17	119.12 (17)
C11—N4—C18	127.68 (16)	C13—C12—C11	119.75 (15)
N1—C1—N2	122.33 (15)	C17—C12—C11	120.98 (16)
N1—C1—S1	115.24 (13)	C12—C13—H13	120.2 (14)
N2—C1—S1	122.42 (12)	C14—C13—C12	120.29 (19)
N1—C2—H2	119.9 (14)	C14—C13—H13	119.5 (14)
C3—C2—N1	117.12 (16)	C13—C14—H14	119.7 (16)
C3—C2—H2	123.0 (14)	C15—C14—C13	119.8 (2)
C2—C3—C19	128.42 (18)	C15—C14—H14	120.4 (16)
C2—C3—S1	109.41 (14)	C14—C15—H15	121 (2)
C19—C3—S1	122.13 (16)	C16—C15—C14	120.7 (2)
N3—C4—C11	120.07 (15)	C16—C15—H15	118 (2)
N3—C4—C5	132.33 (15)	C15—C16—C17	120.2 (2)
C11—C4—C5	107.59 (14)	C15—C16—H16	120.9 (17)
C6—C5—C10	119.65 (15)	C17—C16—H16	118.9 (17)
C6—C5—C4	134.94 (16)	C16—C17—C12	119.9 (2)
C10—C5—C4	105.41 (14)	C16—C17—H17	118.5 (12)
C7—C6—C5	118.10 (19)	C12—C17—H17	121.6 (12)
C7—C6—H6	120.6 (15)	N4—C18—H182	110.1 (16)
C5—C6—H6	121.3 (15)	N4—C18—H183	108.3 (17)
C6—C7—C8	121.6 (2)	H182—C18—H183	116 (3)
C6—C7—H7	119.2 (16)	N4—C18—H181	111.5 (19)
C8—C7—H7	119.2 (16)	H182—C18—H181	104 (2)
C9—C8—C7	121.03 (19)	H183—C18—H181	107 (2)
C9—C8—H8	120.6 (16)	C3—C19—H193	113 (2)
C7—C8—H8	118.3 (16)	C3—C19—H192	111.8 (19)
C8—C9—C10	117.64 (19)	H193—C19—H192	110 (3)
C8—C9—H9	120.4 (15)	C3—C19—H191	112.3 (18)
C10—C9—H9	121.9 (14)	H193—C19—H191	106 (2)
N4—C10—C9	128.80 (17)	H192—C19—H191	103 (2)
C3—S1—C1—N1	−0.12 (15)	C4—C5—C10—C9	−178.63 (17)
C3—S1—C1—N2	178.57 (15)	C5—C6—C7—C8	0.3 (3)
C1—S1—C3—C2	0.76 (15)	C9—C8—C7—C6	0.1 (3)
C1—S1—C3—C19	−177.22 (18)	C7—C8—C9—C10	0.1 (3)
C1—N1—C2—C3	1.2 (3)	N4—C10—C9—C8	−179.68 (18)
N3—N2—C1—N1	−170.58 (16)	C5—C10—C9—C8	−0.6 (3)
N3—N2—C1—S1	10.8 (2)	C4—C11—N4—C10	−0.63 (18)
C4—N3—N2—C1	−176.83 (13)	C12—C11—N4—C10	177.05 (15)
N2—N3—C4—C11	−177.78 (14)	C4—C11—N4—C18	170.57 (18)
N2—N3—C4—C5	1.5 (3)	C12—C11—N4—C18	−11.8 (3)
C11—N4—C10—C9	179.16 (18)	N4—C11—C12—C13	136.47 (17)
C18—N4—C10—C9	7.4 (3)	C4—C11—C12—C13	−46.3 (3)
C11—N4—C10—C5	−0.01 (18)	N4—C11—C12—C17	−48.0 (2)
C18—N4—C10—C5	−171.73 (17)	C4—C11—C12—C17	129.21 (19)

N2—C1—N1—C2	−179.24 (16)	N4—C11—C4—N3	−179.52 (14)
S1—C1—N1—C2	−0.5 (2)	C12—C11—C4—N3	2.9 (3)
C19—C3—C2—N1	176.5 (2)	N4—C11—C4—C5	1.00 (18)
S1—C3—C2—N1	−1.3 (2)	C12—C11—C4—C5	−176.57 (16)
C6—C5—C4—N3	0.1 (3)	C13—C12—C17—C16	0.3 (3)
C10—C5—C4—N3	179.63 (17)	C11—C12—C17—C16	−175.25 (17)
C6—C5—C4—C11	179.47 (19)	C17—C12—C13—C14	−0.5 (3)
C10—C5—C4—C11	−0.97 (17)	C11—C12—C13—C14	175.09 (18)
C10—C5—C6—C7	−0.8 (3)	C12—C13—C14—C15	0.1 (3)
C4—C5—C6—C7	178.67 (19)	C13—C14—C15—C16	0.6 (4)
C6—C5—C10—N4	−179.76 (15)	C17—C16—C15—C14	−0.8 (4)
C4—C5—C10—N4	0.60 (17)	C12—C17—C16—C15	0.4 (3)
C6—C5—C10—C9	1.0 (3)		

Fig. 1

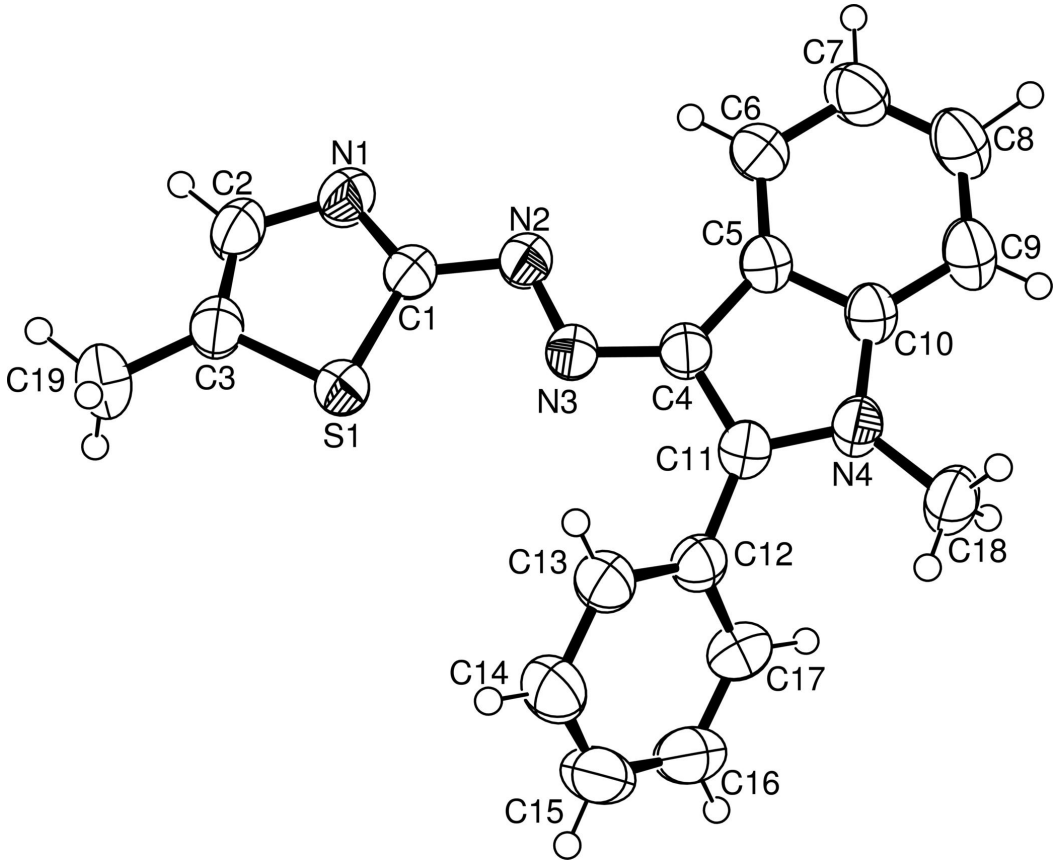
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Fig. 2