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# 3-Methyl-1,4-diphenyl-1*H*-pyrazolo-[3,4-*b*]quinoline

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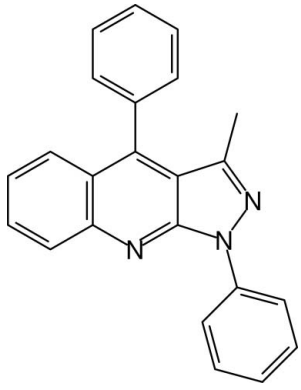
Key indicators: single-crystal X-ray study; $T$ = 293 K, $P$ = 98.6 kPa; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.053; $wR$ factor = 0.139; data-to-parameter ratio = 21.0.

In the title molecule, $C_{23}H_{17}N_3$, the phenyl substituents at positions 1 and 4 are twisted relative to the central core by 27.09 (5) and 66.62 (4)°, respectively. In the crystal, molecules are assembled into centrosymmetric dimers *via* $\pi$–$\pi$ stacking interactions between the 1*H*-pyrazolo[3,4-*b*]quinoline units, with an interplanar distance of 3.601 (2) Å and by weak intermolecular C—H···N interactions.

## Related literature

For the synthesis of 1,3 and 4-substituted 1*H*-pyrazolo[3,4-*b*]quinoline derivatives using Friedländer condensation, see: Danel (1996); Woo *et al.* (2002). For selected photophysical properties of 1*H*-pyrazolo[3,4-*b*]quinoline derivatives, see: Gondek *et al.* (2006). For related structures, see: Szlachcic & Stadnicka (2010); Szlachcic *et al.* (2010).



## Experimental

### Crystal data

$C_{23}H_{17}N_3$
$M_r$ = 335.40
Triclinic, $P\overline{1}$
$a$ = 9.2120 (4) Å
$b$ = 9.9377 (5) Å
$c$ = 10.3440 (4) Å
$\alpha$ = 92.278 (2)°
$\beta$ = 113.376 (2)°
$\gamma$ = 90.152 (2)°
$V$ = 868.37 (7) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.08 mm$^{-1}$
$T$ = 293 K
0.50 × 0.42 × 0.15 mm

### Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min}$ = 0.963, $T_{max}$ = 0.989
6556 measured reflections
4964 independent reflections
3285 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.139
$S$ = 1.02
4964 reflections
236 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C46—H46···N9$^{i}$ | 0.93 | 2.52 | 3.4164 (18) | 163 |

Symmetry code: (i) $-x+1, -y+1, -z$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2306).

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# supplementary materials

*Acta Cryst.* (2010). E**66**, o3009 [ **doi:10.1107/S1600536810042935** ]

# 3-Methyl-1,4-diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline

**P. Szlachcic, A. Danel and K. Stadnicka**

## Comment

The title compound and other 1*H*-pyrazolo[3,4-*b*]quinoline (PQ) derivatives containing hydrogen, methyl or phenyl substituents and their combination, showed important photophysical properties (Gondek *et al.*, 2006) which could be utilized in organic light-emitting diodes (OLED) fabrication. To synthesize 1,3,4-substituted PQ derivatives, a method of preparation introduced by Danel (1996) was used. The results of using the title compound in OLED preparation will be published elsewhere.

The shape of the title molecule is shown in Fig. 1. The core of the molecule, 1*H*-pyrazolo[3,4-*b*]quinoline, is planar and aromatic. The planes of phenyl substituents at positions 1 and 4 are twisted against the core moiety with the torsion angles N2—N1—C11—C16 = -15.7 (2) and C3a—C4—C41—C46 = 116.7 (2)°. The conformation of the molecule is stabilized by two intramolecular interactions of C—H···N type in which N2 and N9 atoms are acceptors.

The packing of the molecules (Fig. 2) is determined by one weak intermolecular hydrogen bond C46—H46···N9 (-*x* + 1, -*y* + 1, -*z*), and π-π interactions: with *Cg*1 (N1—N2—C3—C3a—C9a)···*Cg*3 (C4a—C5—C6—C7—C8—C8a at 1 - *x*, 1 - *y*, -*z*) = 3.731 and *Cg*2 (C3a—C4—C4a—C8a—N9—C9a)···*Cg*2 (C3a—C4—C4a—C8a—N9—C9a at 1 - *x*, 1 - *y*, -*z*) = 3.799 Å resulting in forming molecular dimers. The two C—H···π interactions are described by the geometry parameters (H···A /Å, D···A /Å, <DHA /°, respectively) given below:

C6—H6···*Cg*5 (C41—C42—C43—C44—C45—C46 at 2 - *x*, 1 - *y*, -*z*): 2.967, 3.750, 143;

C31—H31···*Cg*1 (N1—N2—C3—C3a—C9a at 1 - *x*, -*y*, -*z*): 3.172, 3.875, 132.

## Experimental

The title compound was synthesized using procedure already described in literature (Danel, 1996) from 2-aminobenzophenone and 5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one (10 mmol of each substrate, ethylene glycol as a solvent). The product was purified by flash chromatography on $Al_2O_3$ with chloroform as a solvent, followed by crystallization from toluene/petroleum ether to give 2.38 g (71% yield) of light-yellow crystalline solid, mp. 438–440 K. $^1$H NMR ($CDCl_3$): δ 2.14 (s, 3H), 7.25–7.30 (m, 1H), 7.36 (ddd, *J* = 8.6, 6.7, 1.3 Hz, 1H), 7.44–7.47 (m, 2H), 7.52–7.60 (m, 5H). 7.71–7.77 (m, 2H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.49–8.53 (m, 2H). $^{13}$C NMR ($CDCl_3$): δ 14.9, 116.3, 120.3, 123.6, 123.9, 124.9, 127.0, 128.3, 128.7, 129.0 (two signals), 129.7, 130.3, 135.0, 140.0, 143.8, 144.4, 148.5, 150.2. Single crystals suitable for X-ray diffraction were grown by slow evaporation from toluene solution at ambient conditions.

## Refinement

H atoms were included into refinement in geometrically calculated positions, with C—H = 0.93 Å and $U_{iso}$(H) = 1.2$U_{eq}$ for the aromatic CH groups and C—H = 0.96 Å and $U_{iso}$(H) = 1.5$U_{eq}$ for methyl groups. The positions of H atoms were

constrained as a part of a riding model. In the case of methyl group the torsion angle along the $C_{aromatic}$—$C_{methyl}$ bond was refined using AFIX 137 procedure (*SHELXL-97*; Sheldrick, 2008).

**Figures**

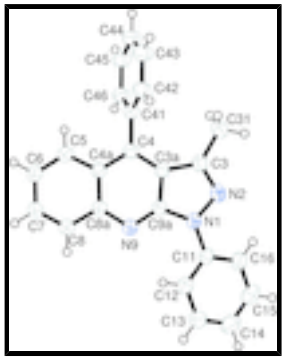

Fig. 1. The conformation of the 3-methyl-1,4-diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline molecule with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Fig. 2. The unit-cell contents of the title compound in projection along [001] showing molecular dimers formation.

**3-Methyl-1,4-diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline**

*Crystal data*

| | |
|---|---|
| $C_{23}H_{17}N_3$ | $Z = 2$ |
| $M_r = 335.40$ | $F(000) = 352$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.283$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Melting point = 438–440 K |
| $a = 9.2120$ (4) Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $b = 9.9377$ (5) Å | Cell parameters from 2458 reflections |
| $c = 10.3440$ (4) Å | $\theta = 1.0$–$30.0°$ |
| $\alpha = 92.278$ (2)° | $\mu = 0.08$ mm$^{-1}$ |
| $\beta = 113.376$ (2)° | $T = 293$ K |
| $\gamma = 90.152$ (2)° | Plate, green–yellow |
| $V = 868.37$ (7) Å$^3$ | 0.50 × 0.42 × 0.15 mm |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer | 4964 independent reflections |
| Radiation source: fine-focus sealed tube | 3285 reflections with $I > 2\sigma(I)$ |
| horizontally mounted graphite crystal | $R_{int} = 0.020$ |
| Detector resolution: 9 pixels mm$^{-1}$ | $\theta_{max} = 30.0°$, $\theta_{min} = 2.9°$ |
| φ and o scans to fill Ewald sphere | $h = -12 \rightarrow 11$ |

Absorption correction: multi-scan (*DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997)

$T_{min}$ = 0.963, $T_{max}$ = 0.989

6556 measured reflections

$k = -13 \rightarrow 7$

$l = -14 \rightarrow 13$

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.053

$wR(F^2)$ = 0.139

$S$ = 1.02

4964 reflections

236 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.1697P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.24 e Å$^{-3}$

$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

*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.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.34388 (14) | 0.18687 (11) | 0.08010 (12) | 0.0397 (3) |
| N2 | 0.28625 (15) | 0.11194 (12) | −0.04633 (13) | 0.0438 (3) |
| C3 | 0.37588 (17) | 0.13841 (14) | −0.11453 (15) | 0.0416 (3) |
| C3A | 0.49700 (16) | 0.23706 (13) | −0.03567 (14) | 0.0351 (3) |
| C4 | 0.61386 (15) | 0.31001 (13) | −0.05685 (14) | 0.0344 (3) |
| C4A | 0.70159 (15) | 0.40697 (13) | 0.05158 (14) | 0.0345 (3) |
| C5 | 0.82339 (17) | 0.49062 (14) | 0.04416 (15) | 0.0418 (3) |
| H5 | 0.8450 | 0.4851 | −0.0364 | 0.050* |
| C6 | 0.90904 (18) | 0.57853 (16) | 0.15214 (17) | 0.0478 (4) |
| H6 | 0.9870 | 0.6330 | 0.1441 | 0.057* |
| C7 | 0.88014 (19) | 0.58731 (16) | 0.27575 (17) | 0.0514 (4) |
| H7 | 0.9402 | 0.6466 | 0.3497 | 0.062* |
| C8 | 0.76495 (18) | 0.50976 (15) | 0.28780 (16) | 0.0464 (4) |
| H8 | 0.7476 | 0.5163 | 0.3704 | 0.056* |
| C8A | 0.67061 (15) | 0.41895 (13) | 0.17655 (14) | 0.0356 (3) |
| N9 | 0.55506 (13) | 0.34765 (11) | 0.19637 (12) | 0.0381 (3) |
| C9A | 0.47232 (15) | 0.26467 (13) | 0.08992 (14) | 0.0343 (3) |

| | | | | |
|---|---|---|---|---|
| C11 | 0.25132 (16) | 0.19574 (13) | 0.16186 (14) | 0.0378 (3) |
| C12 | 0.31890 (19) | 0.24076 (15) | 0.30166 (16) | 0.0487 (4) |
| H12 | 0.4260 | 0.2639 | 0.3436 | 0.058* |
| C13 | 0.2259 (2) | 0.25117 (17) | 0.37876 (19) | 0.0579 (4) |
| H13 | 0.2706 | 0.2831 | 0.4723 | 0.069* |
| C14 | 0.0681 (2) | 0.21477 (17) | 0.3187 (2) | 0.0591 (4) |
| H14 | 0.0064 | 0.2220 | 0.3712 | 0.071* |
| C15 | 0.00234 (19) | 0.16761 (17) | 0.18044 (19) | 0.0553 (4) |
| H15 | −0.1038 | 0.1413 | 0.1401 | 0.066* |
| C16 | 0.09222 (17) | 0.15891 (15) | 0.10080 (17) | 0.0455 (3) |
| H16 | 0.0464 | 0.1285 | 0.0068 | 0.055* |
| C31 | 0.3400 (2) | 0.06994 (18) | −0.25516 (17) | 0.0578 (4) |
| H31A | 0.4209 | 0.0063 | −0.2477 | 0.087* |
| H31B | 0.3365 | 0.1358 | −0.3217 | 0.087* |
| H31C | 0.2395 | 0.0237 | −0.2866 | 0.087* |
| C41 | 0.64981 (16) | 0.28577 (13) | −0.18381 (14) | 0.0357 (3) |
| C42 | 0.70864 (19) | 0.16239 (15) | −0.20626 (16) | 0.0462 (4) |
| H42 | 0.7243 | 0.0953 | −0.1421 | 0.055* |
| C43 | 0.7441 (2) | 0.13829 (17) | −0.32315 (18) | 0.0540 (4) |
| H43 | 0.7836 | 0.0555 | −0.3371 | 0.065* |
| C44 | 0.72084 (19) | 0.23688 (18) | −0.41857 (17) | 0.0524 (4) |
| H44 | 0.7443 | 0.2207 | −0.4973 | 0.063* |
| C45 | 0.66269 (18) | 0.35998 (17) | −0.39743 (16) | 0.0491 (4) |
| H45 | 0.6468 | 0.4265 | −0.4622 | 0.059* |
| C46 | 0.62795 (17) | 0.38491 (14) | −0.28066 (15) | 0.0417 (3) |
| H46 | 0.5898 | 0.4684 | −0.2667 | 0.050* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0428 (6) | 0.0404 (6) | 0.0370 (6) | −0.0120 (5) | 0.0179 (5) | −0.0042 (5) |
| N2 | 0.0489 (7) | 0.0417 (6) | 0.0396 (6) | −0.0131 (5) | 0.0172 (5) | −0.0058 (5) |
| C3 | 0.0461 (8) | 0.0386 (7) | 0.0390 (7) | −0.0073 (6) | 0.0164 (6) | −0.0017 (6) |
| C3A | 0.0399 (7) | 0.0325 (6) | 0.0335 (6) | −0.0019 (5) | 0.0153 (6) | 0.0008 (5) |
| C4 | 0.0363 (7) | 0.0329 (6) | 0.0353 (7) | 0.0014 (5) | 0.0156 (6) | 0.0018 (5) |
| C4A | 0.0342 (7) | 0.0335 (6) | 0.0375 (7) | −0.0004 (5) | 0.0162 (6) | −0.0003 (5) |
| C5 | 0.0409 (8) | 0.0449 (8) | 0.0444 (8) | −0.0061 (6) | 0.0223 (6) | −0.0029 (6) |
| C6 | 0.0417 (8) | 0.0495 (8) | 0.0561 (9) | −0.0134 (6) | 0.0243 (7) | −0.0065 (7) |
| C7 | 0.0485 (9) | 0.0547 (9) | 0.0517 (9) | −0.0176 (7) | 0.0225 (7) | −0.0156 (7) |
| C8 | 0.0461 (8) | 0.0537 (8) | 0.0429 (8) | −0.0131 (7) | 0.0230 (7) | −0.0122 (7) |
| C8A | 0.0351 (7) | 0.0359 (6) | 0.0372 (7) | −0.0031 (5) | 0.0160 (6) | −0.0012 (5) |
| N9 | 0.0389 (6) | 0.0401 (6) | 0.0370 (6) | −0.0073 (5) | 0.0173 (5) | −0.0032 (5) |
| C9A | 0.0359 (7) | 0.0331 (6) | 0.0352 (6) | −0.0033 (5) | 0.0155 (5) | 0.0018 (5) |
| C11 | 0.0420 (7) | 0.0326 (6) | 0.0419 (7) | −0.0047 (5) | 0.0198 (6) | 0.0043 (6) |
| C12 | 0.0521 (9) | 0.0529 (9) | 0.0428 (8) | −0.0151 (7) | 0.0210 (7) | −0.0023 (7) |
| C13 | 0.0749 (12) | 0.0548 (9) | 0.0531 (10) | −0.0144 (8) | 0.0360 (9) | −0.0073 (8) |
| C14 | 0.0658 (11) | 0.0563 (10) | 0.0722 (12) | 0.0003 (8) | 0.0455 (10) | 0.0011 (9) |
| C15 | 0.0425 (9) | 0.0590 (10) | 0.0689 (11) | −0.0006 (7) | 0.0265 (8) | 0.0083 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C16 | 0.0411 (8) | 0.0467 (8) | 0.0467 (8) | −0.0052 (6) | 0.0151 (7) | 0.0040 (7) |
| C31 | 0.0659 (11) | 0.0612 (10) | 0.0460 (9) | −0.0213 (8) | 0.0237 (8) | −0.0155 (8) |
| C41 | 0.0369 (7) | 0.0365 (7) | 0.0355 (7) | −0.0032 (5) | 0.0167 (6) | −0.0012 (6) |
| C42 | 0.0563 (9) | 0.0398 (7) | 0.0454 (8) | 0.0040 (6) | 0.0235 (7) | 0.0007 (6) |
| C43 | 0.0632 (10) | 0.0498 (9) | 0.0546 (10) | 0.0061 (8) | 0.0301 (8) | −0.0069 (8) |
| C44 | 0.0532 (9) | 0.0675 (10) | 0.0417 (8) | −0.0034 (8) | 0.0256 (7) | −0.0085 (8) |
| C45 | 0.0523 (9) | 0.0582 (9) | 0.0403 (8) | −0.0035 (7) | 0.0218 (7) | 0.0067 (7) |
| C46 | 0.0453 (8) | 0.0412 (7) | 0.0421 (8) | 0.0010 (6) | 0.0212 (6) | 0.0029 (6) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| N1—C9A | 1.3790 (16) | C12—C13 | 1.385 (2) |
| N1—N2 | 1.3842 (16) | C12—H12 | 0.9300 |
| N1—C11 | 1.4201 (17) | C13—C14 | 1.376 (3) |
| N2—C3 | 1.3132 (18) | C13—H13 | 0.9300 |
| C3—C3A | 1.4422 (19) | C14—C15 | 1.374 (3) |
| C3—C31 | 1.492 (2) | C14—H14 | 0.9300 |
| C3A—C4 | 1.3885 (18) | C15—C16 | 1.381 (2) |
| C3A—C9A | 1.4217 (18) | C15—H15 | 0.9300 |
| C4—C4A | 1.4249 (18) | C16—H16 | 0.9300 |
| C4—C41 | 1.4876 (18) | C31—H31A | 0.9600 |
| C4A—C5 | 1.4228 (18) | C31—H31B | 0.9600 |
| C4A—C8A | 1.4308 (18) | C31—H31C | 0.9600 |
| C5—C6 | 1.361 (2) | C41—C42 | 1.3898 (19) |
| C5—H5 | 0.9300 | C41—C46 | 1.3907 (19) |
| C6—C7 | 1.405 (2) | C42—C43 | 1.384 (2) |
| C6—H6 | 0.9300 | C42—H42 | 0.9300 |
| C7—C8 | 1.358 (2) | C43—C44 | 1.375 (2) |
| C7—H7 | 0.9300 | C43—H43 | 0.9300 |
| C8—C8A | 1.4190 (19) | C44—C45 | 1.381 (2) |
| C8—H8 | 0.9300 | C44—H44 | 0.9300 |
| C8A—N9 | 1.3631 (16) | C45—C46 | 1.381 (2) |
| N9—C9A | 1.3160 (17) | C45—H45 | 0.9300 |
| C11—C12 | 1.383 (2) | C46—H46 | 0.9300 |
| C11—C16 | 1.3875 (19) | | |
| C9A—N1—N2 | 110.06 (11) | C11—C12—H12 | 120.3 |
| C9A—N1—C11 | 129.37 (11) | C13—C12—H12 | 120.3 |
| N2—N1—C11 | 119.07 (11) | C14—C13—C12 | 120.78 (16) |
| C3—N2—N1 | 108.04 (11) | C14—C13—H13 | 119.6 |
| N2—C3—C3A | 110.55 (12) | C12—C13—H13 | 119.6 |
| N2—C3—C31 | 119.20 (13) | C15—C14—C13 | 119.47 (15) |
| C3A—C3—C31 | 130.23 (13) | C15—C14—H14 | 120.3 |
| C4—C3A—C9A | 118.45 (12) | C13—C14—H14 | 120.3 |
| C4—C3A—C3 | 136.89 (13) | C14—C15—C16 | 120.71 (16) |
| C9A—C3A—C3 | 104.51 (11) | C14—C15—H15 | 119.6 |
| C3A—C4—C4A | 116.60 (12) | C16—C15—H15 | 119.6 |
| C3A—C4—C41 | 122.02 (12) | C15—C16—C11 | 119.61 (15) |
| C4A—C4—C41 | 121.36 (11) | C15—C16—H16 | 120.2 |
| C5—C4A—C4 | 123.14 (12) | C11—C16—H16 | 120.2 |

| | | | |
|---|---|---|---|
| C5—C4A—C8A | 117.71 (12) | C3—C31—H31A | 109.5 |
| C4—C4A—C8A | 119.12 (11) | C3—C31—H31B | 109.5 |
| C6—C5—C4A | 121.57 (13) | H31A—C31—H31B | 109.5 |
| C6—C5—H5 | 119.2 | C3—C31—H31C | 109.5 |
| C4A—C5—H5 | 119.2 | H31A—C31—H31C | 109.5 |
| C5—C6—C7 | 120.27 (13) | H31B—C31—H31C | 109.5 |
| C5—C6—H6 | 119.9 | C42—C41—C46 | 118.74 (12) |
| C7—C6—H6 | 119.9 | C42—C41—C4 | 119.81 (12) |
| C8—C7—C6 | 120.36 (14) | C46—C41—C4 | 121.45 (12) |
| C8—C7—H7 | 119.8 | C43—C42—C41 | 120.68 (14) |
| C6—C7—H7 | 119.8 | C43—C42—H42 | 119.7 |
| C7—C8—C8A | 121.18 (14) | C41—C42—H42 | 119.7 |
| C7—C8—H8 | 119.4 | C44—C43—C42 | 119.96 (14) |
| C8A—C8—H8 | 119.4 | C44—C43—H43 | 120.0 |
| N9—C8A—C8 | 117.20 (12) | C42—C43—H43 | 120.0 |
| N9—C8A—C4A | 123.94 (12) | C43—C44—C45 | 119.95 (14) |
| C8—C8A—C4A | 118.86 (12) | C43—C44—H44 | 120.0 |
| C9A—N9—C8A | 114.32 (11) | C45—C44—H44 | 120.0 |
| N9—C9A—N1 | 125.83 (12) | C46—C45—C44 | 120.36 (14) |
| N9—C9A—C3A | 127.35 (12) | C46—C45—H45 | 119.8 |
| N1—C9A—C3A | 106.81 (11) | C44—C45—H45 | 119.8 |
| C12—C11—C16 | 119.95 (13) | C45—C46—C41 | 120.30 (13) |
| C12—C11—N1 | 120.37 (13) | C45—C46—H46 | 119.9 |
| C16—C11—N1 | 119.67 (13) | C41—C46—H46 | 119.9 |
| C11—C12—C13 | 119.46 (15) | | |
| C9A—N1—N2—C3 | 1.12 (16) | C11—N1—C9A—N9 | 14.3 (2) |
| C11—N1—N2—C3 | 168.47 (12) | N2—N1—C9A—C3A | −0.24 (15) |
| N1—N2—C3—C3A | −1.54 (16) | C11—N1—C9A—C3A | −165.91 (13) |
| N1—N2—C3—C31 | 179.75 (13) | C4—C3A—C9A—N9 | −4.6 (2) |
| N2—C3—C3A—C4 | −173.86 (15) | C3—C3A—C9A—N9 | 179.13 (13) |
| C31—C3—C3A—C4 | 4.7 (3) | C4—C3A—C9A—N1 | 175.65 (12) |
| N2—C3—C3A—C9A | 1.37 (16) | C3—C3A—C9A—N1 | −0.64 (14) |
| C31—C3—C3A—C9A | 179.90 (16) | C9A—N1—C11—C12 | −31.2 (2) |
| C9A—C3A—C4—C4A | 0.62 (18) | N2—N1—C11—C12 | 164.26 (12) |
| C3—C3A—C4—C4A | 175.37 (15) | C9A—N1—C11—C16 | 148.85 (14) |
| C9A—C3A—C4—C41 | 178.75 (12) | N2—N1—C11—C16 | −15.73 (19) |
| C3—C3A—C4—C41 | −6.5 (2) | C16—C11—C12—C13 | −1.3 (2) |
| C3A—C4—C4A—C5 | −179.09 (13) | N1—C11—C12—C13 | 178.74 (13) |
| C41—C4—C4A—C5 | 2.8 (2) | C11—C12—C13—C14 | 1.3 (3) |
| C3A—C4—C4A—C8A | 3.01 (18) | C12—C13—C14—C15 | 0.0 (3) |
| C41—C4—C4A—C8A | −175.13 (12) | C13—C14—C15—C16 | −1.3 (3) |
| C4—C4A—C5—C6 | −177.40 (14) | C14—C15—C16—C11 | 1.3 (2) |
| C8A—C4A—C5—C6 | 0.5 (2) | C12—C11—C16—C15 | 0.0 (2) |
| C4A—C5—C6—C7 | 0.9 (2) | N1—C11—C16—C15 | −179.99 (13) |
| C5—C6—C7—C8 | −1.0 (3) | C3A—C4—C41—C42 | −64.18 (18) |
| C6—C7—C8—C8A | −0.4 (3) | C4A—C4—C41—C42 | 113.86 (15) |
| C7—C8—C8A—N9 | −178.35 (14) | C3A—C4—C41—C46 | 116.72 (15) |
| C7—C8—C8A—C4A | 1.8 (2) | C4A—C4—C41—C46 | −65.24 (18) |
| C5—C4A—C8A—N9 | 178.31 (13) | C46—C41—C42—C43 | −0.3 (2) |

| | | | |
|---|---|---|---|
| C4—C4A—C8A—N9 | −3.7 (2) | C4—C41—C42—C43 | −179.45 (14) |
| C5—C4A—C8A—C8 | −1.87 (19) | C41—C42—C43—C44 | −0.1 (2) |
| C4—C4A—C8A—C8 | 176.15 (13) | C42—C43—C44—C45 | 0.2 (3) |
| C8—C8A—N9—C9A | −179.62 (13) | C43—C44—C45—C46 | 0.1 (2) |
| C4A—C8A—N9—C9A | 0.20 (19) | C44—C45—C46—C41 | −0.6 (2) |
| C8A—N9—C9A—N1 | −176.24 (12) | C42—C41—C46—C45 | 0.7 (2) |
| C8A—N9—C9A—C3A | 4.0 (2) | C4—C41—C46—C45 | 179.80 (13) |
| N2—N1—C9A—N9 | 179.99 (13) | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C12—H12···N9 | 0.93 | 2.44 | 3.0012 (18) | 119 |
| C46—H46···N9$^{i}$ | 0.93 | 2.52 | 3.4164 (18) | 163 |
| C16—H16···N2 | 0.93 | 2.48 | 2.799 (2) | 100 |

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*.

**Fig. 1**

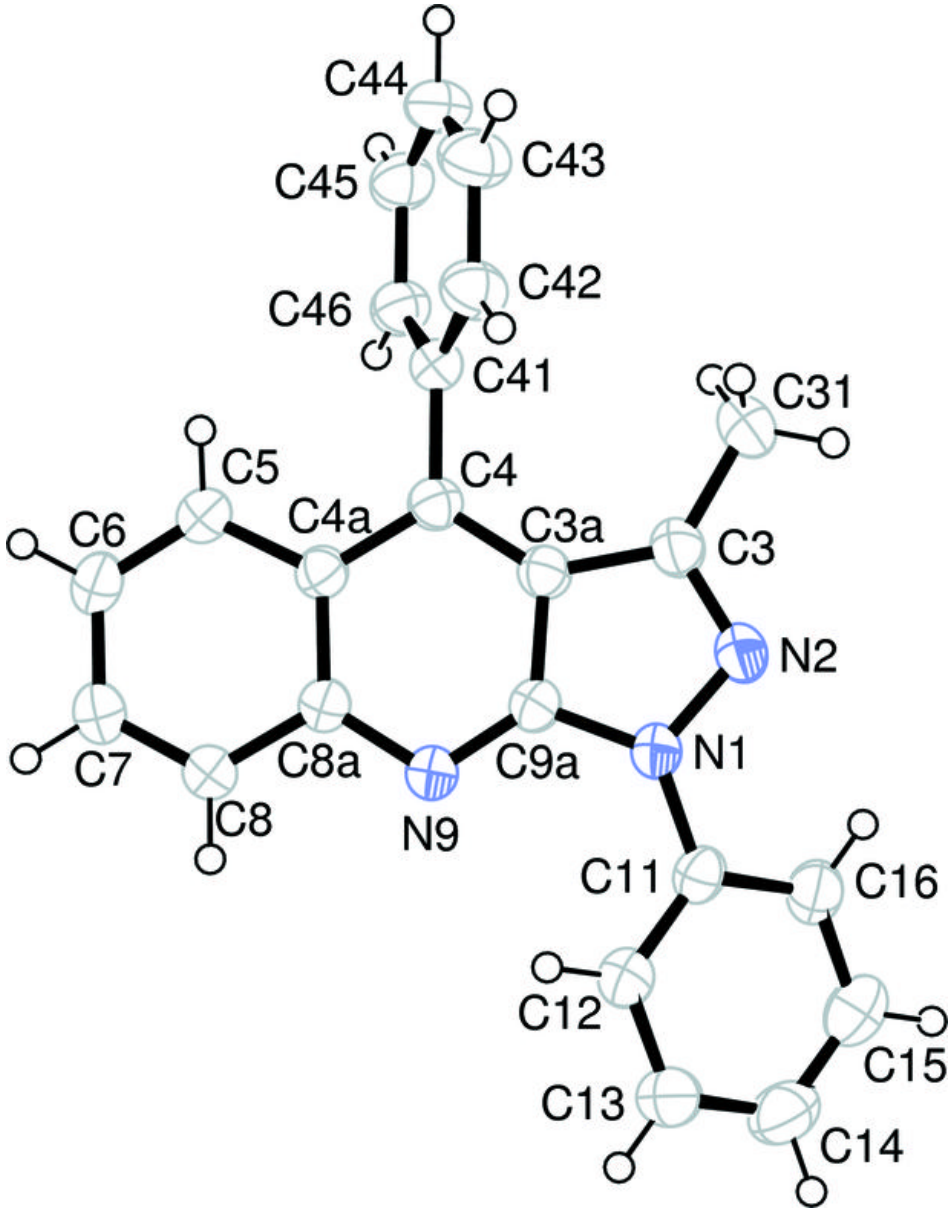
C44
C43
C45
C42
C46
C41
C31
C5
C4
C6
C4a
C3a
C3
N2
C7
C8a
C9a
N1
C8
N9
C11
C16
C12
C15
C13
C14

**Fig. 2**