

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

# 3,5-Bis[1-acetyl-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-3-yl]-2,6-dimethylpyridine

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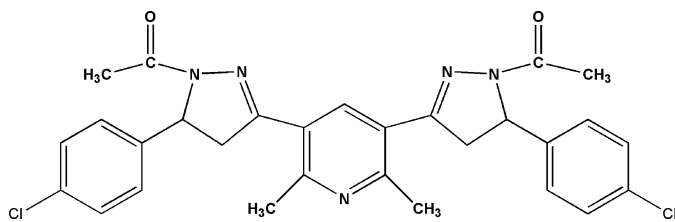
Received 25 July 2008; accepted 28 July 2008

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.037;  $wR$  factor = 0.078; data-to-parameter ratio = 10.9.

The title compound,  $\text{C}_{29}\text{H}_{27}\text{Cl}_2\text{N}_5\text{O}_2$ , contains a central pyridine ring and two functionalized pyrazoline rings. The pyridine ring and the two attached pyrazoline rings are nearly coplanar, whereas the terminal chlorophenyl rings are nearly perpendicular to the attached pyrazoline rings [dihedral angles =  $86.78(1)$  and  $77.70(1)^\circ$ ]. Molecules are linked by weak intermolecular  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonding.

## Related literature

For general background, see: Ahn *et al.* (2004); Palaska *et al.* (1996); Yar *et al.* (2006)



## Experimental

### Crystal data

$\text{C}_{29}\text{H}_{27}\text{Cl}_2\text{N}_5\text{O}_2$   
 $M_r = 548.46$   
Monoclinic,  $P2_1$   
 $a = 12.345(3)$  Å

$b = 9.6763(19)$  Å  
 $c = 13.268(3)$  Å  
 $\beta = 115.00(3)^\circ$   
 $V = 1436.4(5)$  Å<sup>3</sup>

$Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 0.26$  mm<sup>-1</sup>

$T = 296(2)$  K  
 $0.30 \times 0.20 \times 0.20$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.926$ ,  $T_{\max} = 0.950$   
7509 measured reflections  
3736 independent reflections  
2520 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.077$   
 $S = 0.91$   
3736 reflections  
344 parameters  
1 restraint

H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.14$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.15$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983),  
1031 Friedel pairs  
Flack parameter: 0.06 (6)

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                              | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{C9}-\text{H9A}\cdots\text{O2}^i$    | 0.99  | 2.59        | 3.358 (3)   | 135           |
| $\text{C17}-\text{H17A}\cdots\text{O2}^ii$ | 0.95  | 2.50        | 3.359 (4)   | 151           |

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

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

The authors thank the Instrument Analysis and Research Center of Shanghai University for the data collection. The project was supported by the Key Subject of Shanghai Municipal Education Commission (grant No. J50102) and the Foundation of the Education Commission of Shanghai Municipality, China (grant No. 08zz44).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2444).

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**supplementary materials**

*Acta Cryst.* (2008). E64, o1700 [ doi:10.1107/S1600536808023921 ]

### 3,5-Bis[1-acetyl-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-3-yl]-2,6-dimethylpyridine

Q. Qian, J. Zhang, M. Zhang, X. He and Y.-B. Xia

#### Comment

The pyrazoline derivatives are well known nitrogen-containing heterocyclic compounds which show various biological activities and pharmacological properties (Palaska *et al.*, 1996). Some of them can be anti-bacterial and anti-fungal, others are anti-diabetic, anti-inflammatory and also active against many Mycobacterias (Ahn *et al.*, 2004; Yar *et al.*, 2006). As the stereochemistry may be an important modulator of biological activity, the crystal structure of the title compound has been determined.

The molecular structure is shown in Fig. 1. There are two chlorophenyl rings bonded with two pyrazoline rings in *cis*-arrangement, and these two pyrazoline rings are further bonded with the same pyridine ring. The central pyridine ring and two attached pyrazoline rings are nearly coplanar with the dihedral angles of 1.32 (2) and 4.88 (2)°, whereas the dihedral angles between each chlorophenyl plane and the attached pyrazoline planes are 86.78 (1) and 77.70 (1)°.

In the crystal structure, there are weak intermolecular C—H···O hydrogen bonding (Table 1 and Fig. 2).

#### Experimental

2,6-Dimethyl-3,5-di-[3-(4-chloro-phenyl)-acryloyl-pyridine (1 mmol, 0.436 g) and 85% hydrazine hydrate solution (4 mmol, 0.235 g) were dissolved in 5 ml of acetic acid solution. The solution was refluxed for 8 h, and allowed to cool to room temperature. The reaction mixture was poured into crushed ice, then neutralized with dilute sodium hydroxide solution. The solid separated was filtered off, washed with water, dried and recrystallized from ethyl acetate to give a colorless compound in a yield of of 40%. Single crystals suitable for X-ray analysis were obtained from tetrahydrofuran at room temperature.

#### Refinement

All H atoms were placed in calculated positions, with C—H = 0.93–0.99 Å, and included in the final cycles of refinement using a riding model,  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  (for methyl groups) or  $1.2U_{\text{eq}}(\text{C})$  (for others). There is a void of 56 Å<sup>3</sup> in the crystal structure, but no solvent molecule could be located reasonably.

#### Figures

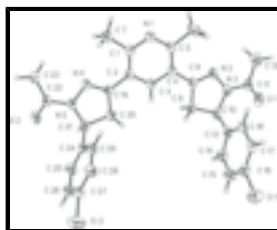


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

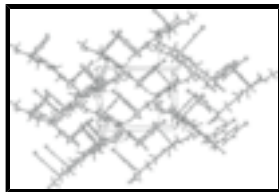


Fig. 2. Crystal packing diagram of compound (I), Hydrogen bonding is indicated by dashed lines.

## 3,5-Bis[1-acetyl-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-3-yl]-2,6-dimethylpyridine

### Crystal data

|                                |   |
|--------------------------------|---|
| $C_{29}H_{27}Cl_2N_5O_2$       | $F_{000} = 572$                           |
| $M_r = 548.46$                 | $D_x = 1.268 \text{ Mg m}^{-3}$           |
| Monoclinic, $P2_1$             | Melting point = 547–549 K                 |
| Hall symbol: P 2yb             | Mo $K\alpha$ radiation                    |
| $a = 12.345 (3) \text{ \AA}$   | $\lambda = 0.71073 \text{ \AA}$           |
| $b = 9.6763 (19) \text{ \AA}$  | Cell parameters from 2029 reflections     |
| $c = 13.268 (3) \text{ \AA}$   | $\theta = 2.7\text{--}20.6^\circ$         |
| $\beta = 115.00 (3)^\circ$     | $\mu = 0.26 \text{ mm}^{-1}$              |
| $V = 1436.4 (5) \text{ \AA}^3$ | $T = 296 (2) \text{ K}$                   |
| $Z = 2$                        | Block, colorless                          |
|                                | $0.30 \times 0.20 \times 0.20 \text{ mm}$ |

### Data collection

|   |  |
|---|--|
| Bruker SMART CCD area-detector diffractometer               | 3736 independent reflections           |
| Radiation source: fine-focus sealed tube                    | 2520 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite                                     | $R_{\text{int}} = 0.027$               |
| $T = 173(2) \text{ K}$                                      | $\theta_{\text{max}} = 25.0^\circ$     |
| $\omega$ scans  | $\theta_{\text{min}} = 2.7^\circ$      |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -14 \rightarrow 14$               |
| $T_{\text{min}} = 0.926$ , $T_{\text{max}} = 0.950$         | $k = -5 \rightarrow 11$                |
| 7509 measured reflections                                   | $l = -15 \rightarrow 15$               |

### Refinement

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full      | H-atom parameters constrained                            |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | $w = 1/[\sigma^2(F_o^2) + (0.0287P)^2]$                  |
| $wR(F^2) = 0.077$               | where $P = (F_o^2 + 2F_c^2)/3$                           |
| $S = 0.91$                      | $(\Delta/\sigma)_{\text{max}} < 0.001$                   |
| 3736 reflections                | $\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$      |
| 344 parameters                  | $\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$     |
| 1 restraint                     | Extinction correction: none                              |
|                                 | Absolute structure: Flack (1983), 1031 Friedel pairs     |

Primary atom site location: structure-invariant direct methods  
 Secondary atom site location: difference Fourier map  
 Flack parameter: 0.06 (6)

*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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )*

|      | <i>x</i>     | <i>y</i>      | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|---------------|---------------|----------------------------------|
| C11  | 0.82566 (10) | 0.19017 (14)  | 0.84787 (9)   | 0.1067 (4)                       |
| C12  | 0.93108 (9)  | -0.23669 (14) | 0.26803 (10)  | 0.1163 (4)                       |
| N4   | 0.3040 (2)   | 0.0470 (3)    | -0.03488 (19) | 0.0535 (7)                       |
| O2   | 0.4646 (2)   | 0.0216 (3)    | -0.19685 (16) | 0.0699 (7)                       |
| N2   | 0.2426 (2)   | 0.4329 (3)    | 0.4064 (2)    | 0.0591 (7)                       |
| C3   | 0.3001 (3)   | 0.2513 (3)    | 0.1935 (2)    | 0.0518 (8)                       |
| H3A  | 0.3772       | 0.2901        | 0.2141        | 0.062*                           |
| C2   | 0.2559 (3)   | 0.1586 (3)    | 0.1053 (2)    | 0.0472 (8)                       |
| N5   | 0.3995 (2)   | 0.0474 (3)    | -0.06575 (19) | 0.0520 (7)                       |
| N1   | 0.0772 (2)   | 0.1372 (3)    | 0.1322 (2)    | 0.0595 (7)                       |
| C8   | 0.2922 (3)   | 0.3870 (3)    | 0.3447 (2)    | 0.0511 (8)                       |
| N3   | 0.3251 (2)   | 0.5240 (3)    | 0.4848 (2)    | 0.0588 (7)                       |
| C21  | 0.5046 (3)   | 0.1276 (3)    | 0.0106 (2)    | 0.0498 (8)                       |
| H21A | 0.5260       | 0.1990        | -0.0324       | 0.060*                           |
| C1   | 0.1420 (3)   | 0.1018 (3)    | 0.0771 (2)    | 0.0533 (8)                       |
| C4   | 0.2348 (3)   | 0.2885 (3)    | 0.2519 (2)    | 0.0501 (8)                       |
| C19  | 0.3333 (3)   | 0.1291 (3)    | 0.0493 (2)    | 0.0474 (8)                       |
| C20  | 0.4534 (2)   | 0.1978 (3)    | 0.0844 (2)    | 0.0503 (8)                       |
| H20A | 0.5048       | 0.1814        | 0.1641        | 0.060*                           |
| H20B | 0.4447       | 0.2986        | 0.0705        | 0.060*                           |
| C13  | 0.5391 (3)   | 0.4494 (3)    | 0.5838 (3)    | 0.0547 (8)                       |
| C24  | 0.6109 (2)   | 0.0369 (3)    | 0.0729 (2)    | 0.0475 (8)                       |
| O1   | 0.3715 (2)   | 0.6813 (3)    | 0.6201 (2)    | 0.0844 (8)                       |
| C7   | 0.0821 (3)   | -0.0002 (4)   | -0.0160 (3)   | 0.0701 (10)                      |
| H7A  | 0.0072       | -0.0321       | -0.0150       | 0.105*                           |
| H7B  | 0.1351       | -0.0793       | -0.0061       | 0.105*                           |
| H7C  | 0.0650       | 0.0446        | -0.0874       | 0.105*                           |
| C29  | 0.6086 (3)   | -0.0608 (4)   | 0.1481 (3)    | 0.0580 (9)                       |
| H29A | 0.5379       | -0.0706       | 0.1593        | 0.070*                           |
| C11  | 0.2948 (4)   | 0.6055 (4)    | 0.5529 (3)    | 0.0677 (10)                      |

## supplementary materials

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|      |            |             |             |             |
|------|------------|-------------|-------------|-------------|
| C9   | 0.4157 (3) | 0.4450 (3)  | 0.3751 (2)  | 0.0564 (9)  |
| H9A  | 0.4160     | 0.5088      | 0.3169      | 0.068*      |
| H9B  | 0.4743     | 0.3702      | 0.3860      | 0.068*      |
| C18  | 0.5107 (3) | 0.3598 (4)  | 0.6500 (3)  | 0.0598 (9)  |
| H18A | 0.4298     | 0.3507      | 0.6388      | 0.072*      |
| C10  | 0.4435 (3) | 0.5226 (4)  | 0.4848 (2)  | 0.0578 (9)  |
| H10A | 0.4694     | 0.6193      | 0.4797      | 0.069*      |
| C25  | 0.7154 (3) | 0.0477 (4)  | 0.0600 (3)  | 0.0642 (10) |
| H25A | 0.7208     | 0.1143      | 0.0097      | 0.077*      |
| C17  | 0.5992 (3) | 0.2823 (4)  | 0.7333 (3)  | 0.0667 (9)  |
| H17A | 0.5787     | 0.2220      | 0.7790      | 0.080*      |
| C22  | 0.3836 (3) | 0.0014 (3)  | -0.1681 (3) | 0.0563 (9)  |
| C28  | 0.7057 (3) | -0.1451 (4) | 0.2079 (3)  | 0.0667 (10) |
| H28A | 0.7016     | -0.2112     | 0.2591      | 0.080*      |
| C14  | 0.6579 (3) | 0.4611 (4)  | 0.6040 (3)  | 0.0742 (11) |
| H14A | 0.6801     | 0.5241      | 0.5611      | 0.089*      |
| C27  | 0.8074 (3) | -0.1310 (4) | 0.1916 (3)  | 0.0684 (10) |
| C6   | 0.0396 (3) | 0.2566 (5)  | 0.2730 (3)  | 0.0917 (14) |
| H6A  | -0.0334    | 0.2013      | 0.2372      | 0.138*      |
| H6B  | 0.0187     | 0.3549      | 0.2660      | 0.138*      |
| H6C  | 0.0800     | 0.2318      | 0.3519      | 0.138*      |
| C5   | 0.1217 (3) | 0.2283 (3)  | 0.2175 (3)  | 0.0572 (9)  |
| C16  | 0.7161 (3) | 0.2940 (4)  | 0.7486 (3)  | 0.0690 (10) |
| C26  | 0.8133 (3) | -0.0363 (5) | 0.1185 (3)  | 0.0753 (11) |
| H26A | 0.8842     | -0.0276     | 0.1074      | 0.090*      |
| C15  | 0.7466 (3) | 0.3822 (5)  | 0.6863 (3)  | 0.0814 (12) |
| H15A | 0.8277     | 0.3908      | 0.6980      | 0.098*      |
| C12  | 0.1685 (3) | 0.5944 (5)  | 0.5398 (3)  | 0.0878 (12) |
| H12A | 0.1567     | 0.6570      | 0.5924      | 0.132*      |
| H12B | 0.1525     | 0.4992      | 0.5548      | 0.132*      |
| H12C | 0.1136     | 0.6197      | 0.4637      | 0.132*      |
| C23  | 0.2705 (3) | -0.0739 (4) | -0.2390 (3) | 0.0778 (11) |
| H23A | 0.2731     | -0.1018     | -0.3089     | 0.117*      |
| H23B | 0.2019     | -0.0129     | -0.2548     | 0.117*      |
| H23C | 0.2629     | -0.1561     | -0.1994     | 0.117*      |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| C11 | 0.0941 (8)  | 0.1130 (9)  | 0.1006 (8)  | 0.0245 (7)   | 0.0290 (6)  | 0.0137 (7)   |
| C12 | 0.0693 (7)  | 0.1272 (11) | 0.1354 (10) | 0.0249 (7)   | 0.0267 (6)  | 0.0115 (8)   |
| N4  | 0.0520 (16) | 0.065 (2)   | 0.0518 (16) | -0.0009 (14) | 0.0295 (13) | -0.0093 (15) |
| O2  | 0.0865 (17) | 0.0762 (18) | 0.0682 (15) | -0.0036 (13) | 0.0531 (14) | -0.0109 (13) |
| N2  | 0.0685 (18) | 0.064 (2)   | 0.0524 (16) | 0.0096 (16)  | 0.0333 (15) | -0.0045 (15) |
| C3  | 0.0518 (18) | 0.058 (2)   | 0.0517 (18) | -0.0006 (17) | 0.0278 (16) | -0.0058 (17) |
| C2  | 0.0498 (18) | 0.051 (2)   | 0.0464 (18) | 0.0020 (15)  | 0.0262 (16) | -0.0037 (16) |
| N5  | 0.0536 (16) | 0.0614 (19) | 0.0479 (15) | -0.0026 (14) | 0.0282 (13) | -0.0081 (14) |
| N1  | 0.0504 (16) | 0.070 (2)   | 0.0659 (18) | -0.0028 (14) | 0.0323 (15) | -0.0081 (16) |

|     |             |             |             |              |             |              |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| C8  | 0.063 (2)   | 0.051 (2)   | 0.0437 (18) | 0.0075 (17)  | 0.0274 (17) | -0.0005 (16) |
| N3  | 0.0655 (18) | 0.062 (2)   | 0.0556 (16) | 0.0036 (15)  | 0.0319 (15) | -0.0152 (15) |
| C21 | 0.0572 (19) | 0.050 (2)   | 0.0508 (18) | -0.0131 (17) | 0.0315 (16) | -0.0076 (17) |
| C1  | 0.0519 (19) | 0.059 (2)   | 0.0488 (19) | -0.0016 (17) | 0.0213 (16) | -0.0033 (17) |
| C4  | 0.060 (2)   | 0.050 (2)   | 0.0499 (19) | 0.0034 (17)  | 0.0320 (16) | 0.0011 (17)  |
| C19 | 0.0526 (19) | 0.047 (2)   | 0.0435 (18) | 0.0018 (16)  | 0.0214 (15) | -0.0054 (16) |
| C20 | 0.0570 (19) | 0.051 (2)   | 0.0503 (18) | -0.0052 (16) | 0.0297 (16) | -0.0076 (17) |
| C13 | 0.067 (2)   | 0.051 (2)   | 0.054 (2)   | -0.0064 (18) | 0.0341 (18) | -0.0127 (17) |
| C24 | 0.0502 (19) | 0.049 (2)   | 0.0514 (19) | -0.0069 (17) | 0.0292 (16) | -0.0083 (17) |
| O1  | 0.109 (2)   | 0.0778 (19) | 0.0720 (17) | 0.0029 (17)  | 0.0441 (16) | -0.0235 (16) |
| C7  | 0.065 (2)   | 0.077 (3)   | 0.076 (2)   | -0.013 (2)   | 0.037 (2)   | -0.018 (2)   |
| C29 | 0.052 (2)   | 0.063 (2)   | 0.067 (2)   | -0.0037 (18) | 0.0330 (18) | -0.006 (2)   |
| C11 | 0.084 (3)   | 0.066 (3)   | 0.057 (2)   | 0.021 (2)    | 0.034 (2)   | -0.002 (2)   |
| C9  | 0.075 (2)   | 0.052 (2)   | 0.052 (2)   | -0.0078 (18) | 0.0363 (18) | -0.0114 (17) |
| C18 | 0.064 (2)   | 0.066 (3)   | 0.061 (2)   | -0.0023 (19) | 0.0382 (19) | -0.0068 (19) |
| C10 | 0.071 (2)   | 0.055 (2)   | 0.056 (2)   | -0.0092 (19) | 0.0355 (19) | -0.0090 (18) |
| C25 | 0.066 (2)   | 0.070 (3)   | 0.072 (2)   | -0.008 (2)   | 0.043 (2)   | -0.001 (2)   |
| C17 | 0.085 (3)   | 0.066 (3)   | 0.066 (2)   | 0.004 (2)    | 0.047 (2)   | 0.001 (2)    |
| C22 | 0.067 (2)   | 0.054 (2)   | 0.052 (2)   | 0.0047 (18)  | 0.0293 (19) | -0.0077 (17) |
| C28 | 0.070 (2)   | 0.069 (3)   | 0.071 (2)   | -0.002 (2)   | 0.039 (2)   | 0.002 (2)    |
| C14 | 0.079 (3)   | 0.078 (3)   | 0.080 (3)   | -0.020 (2)   | 0.047 (2)   | -0.001 (2)   |
| C27 | 0.051 (2)   | 0.076 (3)   | 0.073 (2)   | 0.003 (2)    | 0.0206 (19) | -0.009 (2)   |
| C6  | 0.075 (2)   | 0.126 (4)   | 0.101 (3)   | -0.013 (3)   | 0.063 (2)   | -0.034 (3)   |
| C5  | 0.053 (2)   | 0.068 (3)   | 0.059 (2)   | 0.0039 (18)  | 0.0314 (17) | -0.0082 (19) |
| C16 | 0.069 (2)   | 0.072 (3)   | 0.062 (2)   | 0.003 (2)    | 0.025 (2)   | -0.006 (2)   |
| C26 | 0.054 (2)   | 0.092 (3)   | 0.092 (3)   | -0.007 (2)   | 0.042 (2)   | -0.010 (2)   |
| C15 | 0.064 (3)   | 0.090 (3)   | 0.095 (3)   | -0.007 (2)   | 0.039 (2)   | 0.005 (3)    |
| C12 | 0.087 (3)   | 0.101 (3)   | 0.082 (3)   | 0.027 (2)    | 0.042 (2)   | -0.015 (2)   |
| C23 | 0.076 (2)   | 0.088 (3)   | 0.069 (2)   | -0.005 (2)   | 0.030 (2)   | -0.032 (2)   |

*Geometric parameters (Å, °)*

|         |           |          |           |
|---------|-----------|----------|-----------|
| C11—C16 | 1.752 (4) | C7—H7B   | 0.9800    |
| C12—C27 | 1.760 (4) | C7—H7C   | 0.9800    |
| N4—C19  | 1.291 (3) | C29—C28  | 1.389 (4) |
| N4—N5   | 1.401 (3) | C29—H29A | 0.9500    |
| O2—C22  | 1.227 (3) | C11—C12  | 1.498 (5) |
| N2—C8   | 1.291 (3) | C9—C10   | 1.543 (4) |
| N2—N3   | 1.415 (3) | C9—H9A   | 0.9900    |
| C3—C4   | 1.382 (4) | C9—H9B   | 0.9900    |
| C3—C2   | 1.390 (4) | C18—C17  | 1.399 (4) |
| C3—H3A  | 0.9500    | C18—H18A | 0.9500    |
| C2—C1   | 1.406 (4) | C10—H10A | 1.0000    |
| C2—C19  | 1.465 (4) | C25—C26  | 1.390 (5) |
| N5—C22  | 1.362 (4) | C25—H25A | 0.9500    |
| N5—C21  | 1.484 (3) | C17—C16  | 1.374 (4) |
| N1—C1   | 1.336 (3) | C17—H17A | 0.9500    |
| N1—C5   | 1.355 (4) | C22—C23  | 1.502 (4) |
| C8—C4   | 1.480 (4) | C28—C27  | 1.367 (4) |

## supplementary materials

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|              |           |              |           |
|--------------|-----------|--------------|-----------|
| C8—C9        | 1.511 (4) | C28—H28A     | 0.9500    |
| N3—C11       | 1.365 (4) | C14—C15      | 1.400 (5) |
| N3—C10       | 1.460 (4) | C14—H14A     | 0.9500    |
| C21—C24      | 1.502 (4) | C27—C26      | 1.359 (5) |
| C21—C20      | 1.530 (4) | C6—C5        | 1.509 (4) |
| C21—H21A     | 1.0000    | C6—H6A       | 0.9800    |
| C1—C7        | 1.508 (4) | C6—H6B       | 0.9800    |
| C4—C5        | 1.399 (4) | C6—H6C       | 0.9800    |
| C19—C20      | 1.508 (4) | C16—C15      | 1.348 (5) |
| C20—H20A     | 0.9900    | C26—H26A     | 0.9500    |
| C20—H20B     | 0.9900    | C15—H15A     | 0.9500    |
| C13—C18      | 1.381 (4) | C12—H12A     | 0.9800    |
| C13—C14      | 1.380 (4) | C12—H12B     | 0.9800    |
| C13—C10      | 1.519 (4) | C12—H12C     | 0.9800    |
| C24—C25      | 1.376 (4) | C23—H23A     | 0.9800    |
| C24—C29      | 1.384 (4) | C23—H23B     | 0.9800    |
| O1—C11       | 1.231 (4) | C23—H23C     | 0.9800    |
| C7—H7A       | 0.9800    |              |           |
| C19—N4—N5    | 106.8 (2) | C8—C9—H9B    | 111.1     |
| C8—N2—N3     | 107.0 (3) | C10—C9—H9B   | 111.1     |
| C4—C3—C2     | 121.8 (3) | H9A—C9—H9B   | 109.1     |
| C4—C3—H3A    | 119.1     | C13—C18—C17  | 121.0 (3) |
| C2—C3—H3A    | 119.1     | C13—C18—H18A | 119.5     |
| C3—C2—C1     | 117.9 (2) | C17—C18—H18A | 119.5     |
| C3—C2—C19    | 116.4 (3) | N3—C10—C13   | 114.6 (3) |
| C1—C2—C19    | 125.6 (3) | N3—C10—C9    | 100.4 (2) |
| C22—N5—N4    | 120.4 (3) | C13—C10—C9   | 111.7 (3) |
| C22—N5—C21   | 124.5 (3) | N3—C10—H10A  | 109.9     |
| N4—N5—C21    | 113.8 (2) | C13—C10—H10A | 109.9     |
| C1—N1—C5     | 119.9 (3) | C9—C10—H10A  | 109.9     |
| N2—C8—C4     | 124.1 (3) | C24—C25—C26  | 121.8 (3) |
| N2—C8—C9     | 113.5 (3) | C24—C25—H25A | 119.1     |
| C4—C8—C9     | 122.4 (3) | C26—C25—H25A | 119.1     |
| C11—N3—N2    | 122.1 (3) | C16—C17—C18  | 119.6 (3) |
| C11—N3—C10   | 124.0 (3) | C16—C17—H17A | 120.2     |
| N2—N3—C10    | 113.8 (2) | C18—C17—H17A | 120.2     |
| N5—C21—C24   | 112.2 (2) | O2—C22—N5    | 117.7 (3) |
| N5—C21—C20   | 101.0 (2) | O2—C22—C23   | 123.1 (3) |
| C24—C21—C20  | 114.1 (2) | N5—C22—C23   | 119.1 (3) |
| N5—C21—H21A  | 109.7     | C27—C28—C29  | 118.7 (3) |
| C24—C21—H21A | 109.7     | C27—C28—H28A | 120.7     |
| C20—C21—H21A | 109.7     | C29—C28—H28A | 120.7     |
| N1—C1—C2     | 121.2 (3) | C13—C14—C15  | 121.6 (3) |
| N1—C1—C7     | 114.6 (3) | C13—C14—H14A | 119.2     |
| C2—C1—C7     | 124.2 (3) | C15—C14—H14A | 119.2     |
| C3—C4—C5     | 116.5 (3) | C26—C27—C28  | 120.7 (3) |
| C3—C4—C8     | 116.6 (3) | C26—C27—Cl2  | 120.5 (3) |
| C5—C4—C8     | 126.9 (3) | C28—C27—Cl2  | 118.8 (3) |
| N4—C19—C2    | 123.7 (3) | C5—C6—H6A    | 109.5     |

|                |            |                 |            |
|----------------|------------|-----------------|------------|
| N4—C19—C20     | 114.7 (2)  | C5—C6—H6B       | 109.5      |
| C2—C19—C20     | 121.6 (3)  | H6A—C6—H6B      | 109.5      |
| C19—C20—C21    | 103.0 (2)  | C5—C6—H6C       | 109.5      |
| C19—C20—H20A   | 111.2      | H6A—C6—H6C      | 109.5      |
| C21—C20—H20A   | 111.2      | H6B—C6—H6C      | 109.5      |
| C19—C20—H20B   | 111.2      | N1—C5—C4        | 122.7 (3)  |
| C21—C20—H20B   | 111.2      | N1—C5—C6        | 114.0 (3)  |
| H20A—C20—H20B  | 109.1      | C4—C5—C6        | 123.3 (3)  |
| C18—C13—C14    | 117.5 (3)  | C15—C16—C17     | 120.6 (3)  |
| C18—C13—C10    | 121.9 (3)  | C15—C16—Cl1     | 119.8 (3)  |
| C14—C13—C10    | 120.3 (3)  | C17—C16—Cl1     | 119.5 (3)  |
| C25—C24—C29    | 116.6 (3)  | C27—C26—C25     | 119.8 (3)  |
| C25—C24—C21    | 122.3 (3)  | C27—C26—H26A    | 120.1      |
| C29—C24—C21    | 121.1 (3)  | C25—C26—H26A    | 120.1      |
| C1—C7—H7A      | 109.5      | C16—C15—C14     | 119.6 (3)  |
| C1—C7—H7B      | 109.5      | C16—C15—H15A    | 120.2      |
| H7A—C7—H7B     | 109.5      | C14—C15—H15A    | 120.2      |
| C1—C7—H7C      | 109.5      | C11—C12—H12A    | 109.5      |
| H7A—C7—H7C     | 109.5      | C11—C12—H12B    | 109.5      |
| H7B—C7—H7C     | 109.5      | H12A—C12—H12B   | 109.5      |
| C28—C29—C24    | 122.5 (3)  | C11—C12—H12C    | 109.5      |
| C28—C29—H29A   | 118.7      | H12A—C12—H12C   | 109.5      |
| C24—C29—H29A   | 118.7      | H12B—C12—H12C   | 109.5      |
| O1—C11—N3      | 118.8 (3)  | C22—C23—H23A    | 109.5      |
| O1—C11—C12     | 124.8 (3)  | C22—C23—H23B    | 109.5      |
| N3—C11—C12     | 116.4 (3)  | H23A—C23—H23B   | 109.5      |
| C8—C9—C10      | 103.2 (2)  | C22—C23—H23C    | 109.5      |
| C8—C9—H9A      | 111.1      | H23A—C23—H23C   | 109.5      |
| C10—C9—H9A     | 111.1      | H23B—C23—H23C   | 109.5      |
| C4—C3—C2—C1    | -0.5 (5)   | N2—N3—C11—C12   | -0.4 (5)   |
| C4—C3—C2—C19   | 179.3 (3)  | C10—N3—C11—C12  | 179.1 (3)  |
| C19—N4—N5—C22  | -162.3 (3) | N2—C8—C9—C10    | 8.9 (3)    |
| C19—N4—N5—C21  | 5.3 (3)    | C4—C8—C9—C10    | -171.8 (3) |
| N3—N2—C8—C4    | -179.9 (3) | C14—C13—C18—C17 | -1.0 (5)   |
| N3—N2—C8—C9    | -0.6 (3)   | C10—C13—C18—C17 | 173.1 (3)  |
| C8—N2—N3—C11   | 170.7 (3)  | C11—N3—C10—C13  | 74.2 (4)   |
| C8—N2—N3—C10   | -8.9 (3)   | N2—N3—C10—C13   | -106.2 (3) |
| C22—N5—C21—C24 | -79.9 (4)  | C11—N3—C10—C9   | -165.9 (3) |
| N4—N5—C21—C24  | 113.0 (3)  | N2—N3—C10—C9    | 13.7 (3)   |
| C22—N5—C21—C20 | 158.2 (3)  | C18—C13—C10—N3  | 17.2 (4)   |
| N4—N5—C21—C20  | -8.9 (3)   | C14—C13—C10—N3  | -168.8 (3) |
| C5—N1—C1—C2    | -0.6 (5)   | C18—C13—C10—C9  | -96.1 (3)  |
| C5—N1—C1—C7    | -179.9 (3) | C14—C13—C10—C9  | 77.8 (4)   |
| C3—C2—C1—N1    | 1.0 (4)    | C8—C9—C10—N3    | -12.5 (3)  |
| C19—C2—C1—N1   | -178.8 (3) | C8—C9—C10—C13   | 109.4 (3)  |
| C3—C2—C1—C7    | -179.9 (3) | C29—C24—C25—C26 | 0.7 (5)    |
| C19—C2—C1—C7   | 0.4 (5)    | C21—C24—C25—C26 | 179.7 (3)  |
| C2—C3—C4—C5    | -0.2 (5)   | C13—C18—C17—C16 | -0.9 (5)   |
| C2—C3—C4—C8    | 179.4 (3)  | N4—N5—C22—O2    | 170.1 (3)  |

## supplementary materials

|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| N2—C8—C4—C3     | 179.2 (3)  | C21—N5—C22—O2   | 3.8 (5)    |
| C9—C8—C4—C3     | 0.0 (4)    | N4—N5—C22—C23   | -11.4 (4)  |
| N2—C8—C4—C5     | -1.2 (5)   | C21—N5—C22—C23  | -177.6 (3) |
| C9—C8—C4—C5     | 179.6 (3)  | C24—C29—C28—C27 | -0.1 (5)   |
| N5—N4—C19—C2    | 179.1 (3)  | C18—C13—C14—C15 | 1.9 (5)    |
| N5—N4—C19—C20   | 1.1 (3)    | C10—C13—C14—C15 | -172.3 (3) |
| C3—C2—C19—N4    | -178.9 (3) | C29—C28—C27—C26 | 0.1 (5)    |
| C1—C2—C19—N4    | 0.9 (5)    | C29—C28—C27—C12 | 179.5 (3)  |
| C3—C2—C19—C20   | -1.1 (4)   | C1—N1—C5—C4     | -0.2 (5)   |
| C1—C2—C19—C20   | 178.7 (3)  | C1—N1—C5—C6     | -179.0 (3) |
| N4—C19—C20—C21  | -6.5 (3)   | C3—C4—C5—N1     | 0.6 (5)    |
| C2—C19—C20—C21  | 175.5 (3)  | C8—C4—C5—N1     | -179.0 (3) |
| N5—C21—C20—C19  | 8.4 (3)    | C3—C4—C5—C6     | 179.3 (3)  |
| C24—C21—C20—C19 | -112.2 (3) | C8—C4—C5—C6     | -0.3 (5)   |
| N5—C21—C24—C25  | 116.5 (3)  | C18—C17—C16—C15 | 1.9 (5)    |
| C20—C21—C24—C25 | -129.5 (3) | C18—C17—C16—C11 | -176.6 (3) |
| N5—C21—C24—C29  | -64.7 (4)  | C28—C27—C26—C25 | 0.3 (6)    |
| C20—C21—C24—C29 | 49.4 (4)   | C12—C27—C26—C25 | -179.1 (3) |
| C25—C24—C29—C28 | -0.3 (5)   | C24—C25—C26—C27 | -0.8 (5)   |
| C21—C24—C29—C28 | -179.3 (3) | C17—C16—C15—C14 | -1.0 (6)   |
| N2—N3—C11—O1    | 179.2 (3)  | C11—C16—C15—C14 | 177.5 (3)  |
| C10—N3—C11—O1   | -1.3 (5)   | C13—C14—C15—C16 | -1.0 (6)   |

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

| <i>D</i> —H $\cdots$ <i>A</i>      | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C9—H9A $\cdots$ O2 <sup>i</sup>    | 0.99        | 2.59                | 3.358 (3)                  | 135                           |
| C17—H17A $\cdots$ O2 <sup>ii</sup> | 0.95        | 2.50                | 3.359 (4)                  | 151                           |

Symmetry codes: (i)  $-x+1, y+1/2, -z$ ; (ii)  $x, y, z+1$ .

Fig. 1

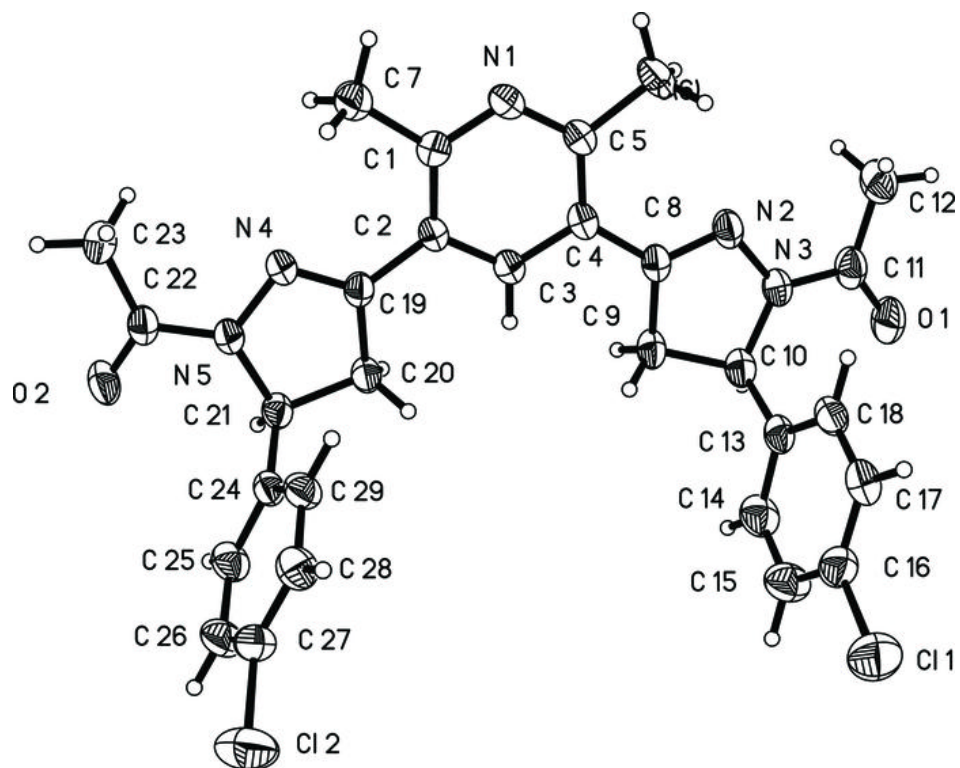


Fig. 2

