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# 1-[(*E*)-2-Formyl-1-(4-methylphenyl)-ethenyl]-3-(4-methylphenyl)pyrazole-4-carbaldehyde

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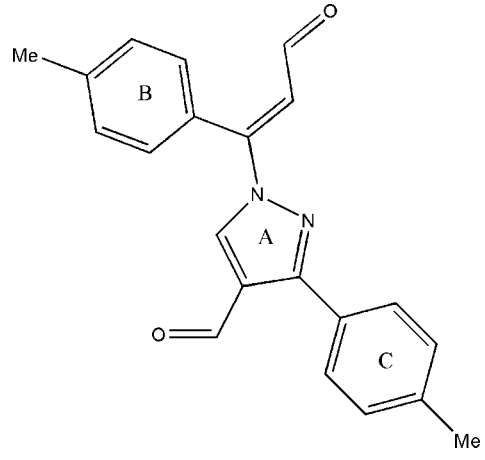
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.055; $wR$ factor = 0.174; data-to-parameter ratio = 26.4.

In the crystal structure of the title compound, $C_{21}H_{18}N_2O_2$, molecules are linked through C—H···O interactions. Two symmetry-related molecules form a cyclic centrosymmetric $R_2^2(20)$ dimer. These dimers are further connected into chains running along the *b* axis.

## Related literature

For related literature, see: Baraldi *et al.* (1998); Bernstein *et al.* (1995); Bruno *et al.* (1990); Chen & Li (1998); Cottineau *et al.* (2002); Londershausen (1996); Mishra *et al.* (1998); Smith *et al.* (2001).




## Experimental

### Crystal data

$C_{21}H_{18}N_2O_2$
$M_r$ = 330.37
Monoclinic, $P2_1/n$
$a$ = 10.2914 (4) Å
$b$ = 15.3618 (5) Å
$c$ = 11.0271 (4) Å
$\beta$ = 98.778 (1)°
$V$ = 1722.90 (11) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.08 mm$^{-1}$
$T$ = 293 (2) K
0.30 × 0.20 × 0.16 mm

### Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min}$ = 0.980, $T_{max}$ = 0.987
24747 measured reflections
6019 independent reflections
3731 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.025

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.174
$S$ = 1.04
6019 reflections
228 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.30 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C22—H22$A$···O2$^{i}$ | 0.96 | 2.60 | 3.378 (2) | 139 |
| C5—H5···O1$^{ii}$ | 0.93 | 2.23 | 3.1094 (17) | 159 |

Symmetry codes: (i) $-x+3, -y, -z$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2774).

## References

Baraldi, P. G., Manfredini, S., Romagnoli, R., Stevanato, L., Zaid, A. N. & Manservigi, R. (1998). *Nucleosides Nucleotides*, **17**, 2165–2171.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2004). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruno, O., Bondavalli, F., Ranise, A., Schenone, P., Losasso, C., Cilenti, L., Matera, C. & Marmo, E. (1990). *Farmaco*, **45**, 147–66.
Chen, H. S. & Li, Z. M. (1998). *Chem. J. Chin. Univ.* **19**, 572–576.
Cottineau, B., Toto, P., Marot, C., Pipaud, A. & Chenault, J. (2002). *Bioorg. Med. Chem.* **12**, 2105–2108.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Londershausen, M. (1996). *Pestic. Sci.* **48**, 269–274.
Mishra, P. D., Wahidullah, S. & Kamat, S. Y. (1998). *Indian J. Chem. Sect. B*, **37**, 199.
Sheldrick, G. M. (2001). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Smith, S. R., Denhardt, G. & Terminelli, C. (2001). *Eur. J. Pharmacol.* **432**, 107–119.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

# supporting information

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## 1-[(*E*)-2-Formyl-1-(4-methylphenyl)ethenyl]-3-(4-methylphenyl)pyrazole-4-carbaldehyde

**P. Ramesh, A. Subbiahpandi, Ramaiyan Manikannan, S. Muthusubramanian and M. N. Ponnuswamy**

### S1. Comment

Pyrazoles and its derivatives have been reported to possess significant antiarrhythmic and sedative (Bruno *et al.*, 1990), hypoglycemic (Cottineau *et al.*, 2002), antiviral (Baraldi *et al.*, 1998), and pesticidal (Londershausen,1996) activities. Some of their derivatives have also been successfully tested for their antifungal (Chen & Li, 1998), antihistaminic (Mishra *et al.*, 1998) and anti-inflammatory (Smith *et al.*, 2001) properties.

The pyrazole ring A and methylphenyl ring C are near-coplanar with the inter-ring dihedral angle of 17.08 (7)°, whereas the pyrazole ring is twisted from the methylphenyl ring B as can be seen from the dihedral angle of 79.70 (8)°. The propenal group assumes an extended conformation which is evidenced from the torsion angle of [N1—C6—C14—C15] -175.47 (12)°.

The crystal structure is stabilized by C—H···O type of intermolecular interactions. Atom C5 at (*x*, *y*, *z*) donates a proton to atom O1 at (3/2 - *x*,-1/2 + *y*,1/2 - *z*) form a one dimensional C7 chain (Bernstein *et al.* 1995) running along *b* axis. The molecules at positions (*x*, *y*, *z*) and (3 - *x*, -*y*, -*z*) form a cyclic centrosymmetric $R_2^2(20)$ dimer through C22—H22A···O2 hydrogen bonds.

### S2. Experimental

A mixture of 1-(4-methylphenyl)-1-ethanone *N*-[(*E*)-1-phenylethylidene] hydrazone (0.003 mole) and 3 ml of dimethyl formamide kept in an ice bath at 0° C, phosphorus oxycholride (0.024 mole) was added dropwise for 5–10 minutes. The reaction mixture was then kept in a microwave oven at 600 W for 30–60 sec. The process of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was poured into crushed ice and extracted with dichloromethane. The organic layer was dried with anhydrous sodium sulfate. The different compounds present in the mixture were separated by column chromatography using petroleum ether and ethyl acetate mixture as eluent. This isolated compound was rectystalized in dichloromethane to obtain 3-(4-methylphenyl)-1-[(*E*)-1-(4-methylphenyl) -3-oxo-1-propenyl]-1*H*-pyrazole-4-carbaldehyde in 57% yield.

### S3. Refinement

H atoms were positioned geometrically (C—H=0.93–0.96 Å) and allowed to ride on their parent atoms, with $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H 1.2$U_{eq}$(C) for other H atoms. The methyl groups were allowed to rotate but not to tip.

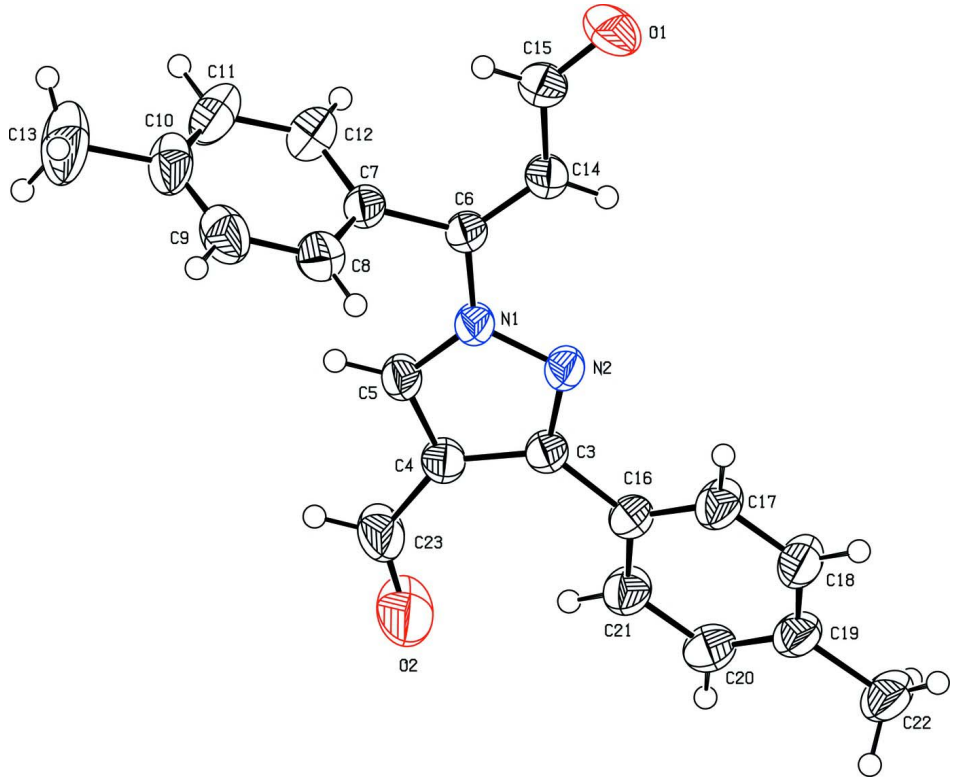


**Figure 1**

Perspective view of the molecules showing the thermal ellipsoids are drawn at 50% probability level. The H atoms are shown as small circles of arbitrary radii.

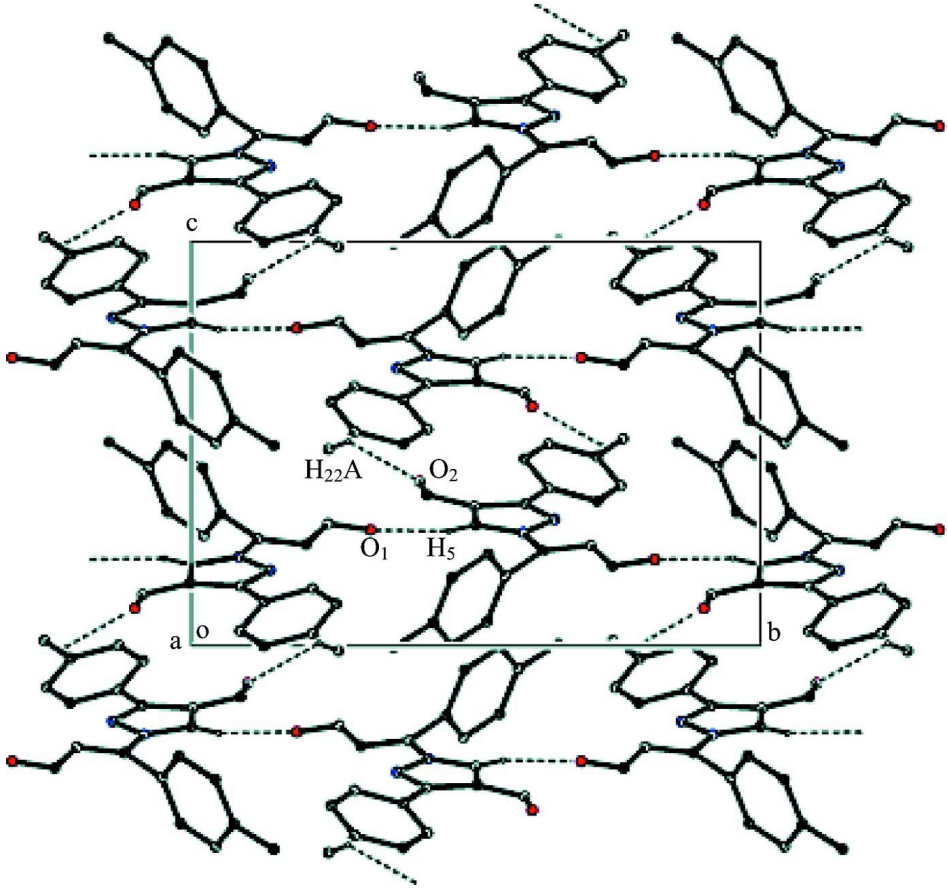


**Figure 2**

Perspective view of the crystal packing showing hydrogen-bond interactions (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity.

**1-[(*E*)-2-Formyl-1-(4-methylphenyl)ethenyl]-3-(4-methylphenyl)pyrazole- 4-carbaldehyde**

*Crystal data*

$C_{21}H_{18}N_2O_2$
$M_r = 330.37$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 10.2914$ (4) Å
$b = 15.3618$ (5) Å
$c = 11.0271$ (4) Å
$\beta = 98.778$ (1)°
$V = 1722.90$ (11) Å$^3$
$Z = 4$
$F(000) = 696$
$D_x = 1.274$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4580 reflections
$\theta = 2.3$–$32.2$°
$\mu = 0.08$ mm$^{-1}$
$T = 293$ K
Block, colorless
0.30 × 0.20 × 0.16 mm

*Data collection*

Bruker APEX2 CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.980$, $T_{max} = 0.987$
24747 measured reflections
6019 independent reflections
3731 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.025
$\theta_{max}$ = 32.3°, $\theta_{min}$ = 2.3°
$h$ = −9→15
$k$ = −22→19
$l$ = −16→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.174
$S$ = 1.04
6019 reflections
228 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0833P)^2 + 0.2417P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.037
$\Delta\rho_{max}$ = 0.35 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.30 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.

**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 (Å²)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.65358 (11) | 0.31462 (7) | 0.28639 (13) | 0.0678 (3) |
| O2 | 1.23915 (18) | −0.09914 (9) | 0.0928 (2) | 0.1340 (9) |
| N1 | 0.93785 (9) | 0.08384 (7) | 0.22048 (10) | 0.0378 (2) |
| N2 | 1.03155 (10) | 0.13820 (7) | 0.18711 (10) | 0.0395 (2) |
| C3 | 1.12006 (11) | 0.08674 (8) | 0.14811 (11) | 0.0367 (3) |
| C4 | 1.08139 (12) | −0.00258 (8) | 0.15437 (12) | 0.0413 (3) |
| C5 | 0.96509 (12) | −0.00004 (8) | 0.20099 (12) | 0.0401 (3) |
| H5 | 0.9144 | −0.0478 | 0.2163 | 0.048* |
| C6 | 0.82656 (11) | 0.11747 (8) | 0.26494 (11) | 0.0367 (3) |
| C7 | 0.75369 (11) | 0.05214 (8) | 0.32683 (12) | 0.0381 (3) |
| C8 | 0.80708 (14) | 0.01954 (10) | 0.44021 (14) | 0.0509 (3) |
| H8 | 0.8884 | 0.0396 | 0.4784 | 0.061* |
| C9 | 0.74082 (17) | −0.04269 (11) | 0.49748 (15) | 0.0593 (4) |
| H9 | 0.7777 | −0.0632 | 0.5744 | 0.071* |
| C10 | 0.62160 (17) | −0.07477 (10) | 0.44295 (16) | 0.0594 (4) |
| C11 | 0.56858 (16) | −0.04197 (12) | 0.33110 (18) | 0.0648 (5) |
| H11 | 0.4876 | −0.0627 | 0.2931 | 0.078* |
| C12 | 0.63277 (14) | 0.02175 (11) | 0.27265 (14) | 0.0527 (4) |
| H12 | 0.5940 | 0.0437 | 0.1971 | 0.063* |
| C13 | 0.5526 (2) | −0.14496 (13) | 0.5044 (2) | 0.0956 (8) |
| H13A | 0.4601 | −0.1432 | 0.4741 | 0.143* |
| H13B | 0.5667 | −0.1356 | 0.5915 | 0.143* |

| | | | | |
|---|---|---|---|---|
| H13C | 0.5872 | −0.2008 | 0.4867 | 0.143* |
| C14 | 0.79599 (12) | 0.20179 (9) | 0.25103 (13) | 0.0438 (3) |
| H14 | 0.8454 | 0.2369 | 0.2066 | 0.053* |
| C15 | 0.68876 (13) | 0.24017 (10) | 0.30271 (14) | 0.0487 (3) |
| H15 | 0.6441 | 0.2053 | 0.3516 | 0.058* |
| C16 | 1.23610 (11) | 0.12790 (9) | 0.10905 (12) | 0.0386 (3) |
| C17 | 1.26700 (13) | 0.21329 (10) | 0.14214 (14) | 0.0497 (3) |
| H17 | 1.2159 | 0.2431 | 0.1911 | 0.060* |
| C18 | 1.37242 (14) | 0.25480 (10) | 0.10352 (15) | 0.0527 (4) |
| H18 | 1.3910 | 0.3122 | 0.1268 | 0.063* |
| C19 | 1.45103 (12) | 0.21259 (10) | 0.03075 (13) | 0.0454 (3) |
| C20 | 1.42132 (13) | 0.12763 (10) | −0.00071 (14) | 0.0503 (3) |
| H20 | 1.4736 | 0.0978 | −0.0486 | 0.060* |
| C21 | 1.31552 (13) | 0.08512 (10) | 0.03692 (13) | 0.0475 (3) |
| H21 | 1.2976 | 0.0276 | 0.0137 | 0.057* |
| C22 | 1.56456 (14) | 0.25876 (12) | −0.01291 (16) | 0.0582 (4) |
| H22A | 1.6425 | 0.2240 | 0.0057 | 0.087* |
| H22B | 1.5783 | 0.3140 | 0.0277 | 0.087* |
| H22C | 1.5451 | 0.2677 | −0.1000 | 0.087* |
| C23 | 1.13601 (18) | −0.08585 (10) | 0.12661 (19) | 0.0684 (5) |
| H23 | 1.0849 | −0.1346 | 0.1362 | 0.082* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0641 (7) | 0.0420 (7) | 0.0968 (9) | 0.0162 (5) | 0.0110 (6) | −0.0076 (6) |
| O2 | 0.1215 (13) | 0.0506 (8) | 0.263 (2) | 0.0205 (8) | 0.1355 (15) | 0.0071 (11) |
| N1 | 0.0371 (5) | 0.0308 (5) | 0.0488 (6) | 0.0001 (4) | 0.0169 (4) | 0.0010 (4) |
| N2 | 0.0387 (5) | 0.0325 (6) | 0.0508 (6) | −0.0020 (4) | 0.0180 (4) | 0.0002 (4) |
| C3 | 0.0366 (5) | 0.0355 (7) | 0.0399 (6) | 0.0009 (4) | 0.0117 (4) | 0.0008 (5) |
| C4 | 0.0424 (6) | 0.0353 (7) | 0.0493 (7) | 0.0019 (5) | 0.0171 (5) | −0.0013 (5) |
| C5 | 0.0433 (6) | 0.0298 (6) | 0.0502 (7) | −0.0006 (5) | 0.0167 (5) | −0.0007 (5) |
| C6 | 0.0337 (5) | 0.0343 (6) | 0.0442 (6) | 0.0010 (4) | 0.0129 (5) | 0.0013 (5) |
| C7 | 0.0373 (5) | 0.0332 (6) | 0.0470 (7) | 0.0008 (4) | 0.0166 (5) | 0.0000 (5) |
| C8 | 0.0489 (7) | 0.0486 (8) | 0.0561 (8) | 0.0020 (6) | 0.0110 (6) | 0.0086 (6) |
| C9 | 0.0766 (10) | 0.0492 (9) | 0.0572 (9) | 0.0087 (8) | 0.0266 (8) | 0.0136 (7) |
| C10 | 0.0757 (10) | 0.0409 (8) | 0.0730 (11) | −0.0059 (7) | 0.0476 (8) | −0.0042 (7) |
| C11 | 0.0556 (8) | 0.0655 (11) | 0.0784 (12) | −0.0242 (8) | 0.0266 (8) | −0.0120 (9) |
| C12 | 0.0471 (7) | 0.0578 (9) | 0.0545 (8) | −0.0103 (6) | 0.0115 (6) | 0.0000 (7) |
| C13 | 0.1297 (19) | 0.0620 (12) | 0.1154 (18) | −0.0239 (12) | 0.0837 (15) | −0.0010 (11) |
| C14 | 0.0411 (6) | 0.0357 (7) | 0.0578 (8) | 0.0027 (5) | 0.0176 (6) | 0.0040 (6) |
| C15 | 0.0424 (6) | 0.0409 (8) | 0.0647 (9) | 0.0053 (5) | 0.0145 (6) | −0.0028 (6) |
| C16 | 0.0360 (5) | 0.0412 (7) | 0.0404 (6) | −0.0007 (5) | 0.0113 (5) | 0.0016 (5) |
| C17 | 0.0474 (7) | 0.0471 (8) | 0.0599 (9) | −0.0060 (6) | 0.0247 (6) | −0.0076 (6) |
| C18 | 0.0500 (7) | 0.0461 (8) | 0.0661 (9) | −0.0105 (6) | 0.0221 (7) | −0.0054 (7) |
| C19 | 0.0356 (6) | 0.0564 (9) | 0.0455 (7) | −0.0020 (5) | 0.0102 (5) | 0.0086 (6) |
| C20 | 0.0445 (7) | 0.0573 (9) | 0.0537 (8) | 0.0025 (6) | 0.0216 (6) | −0.0006 (6) |
| C21 | 0.0459 (7) | 0.0447 (8) | 0.0556 (8) | −0.0015 (5) | 0.0198 (6) | −0.0052 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C22 | 0.0425 (7) | 0.0709 (11) | 0.0644 (9) | −0.0070 (7) | 0.0180 (6) | 0.0116 (8) |
| C23 | 0.0755 (11) | 0.0359 (8) | 0.1052 (14) | 0.0070 (7) | 0.0502 (10) | 0.0005 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C15 | 1.2048 (17) | C12—H12 | 0.9300 |
| O2—C23 | 1.1949 (19) | C13—H13A | 0.9600 |
| N1—C5 | 1.3429 (16) | C13—H13B | 0.9600 |
| N1—N2 | 1.3679 (13) | C13—H13C | 0.9600 |
| N1—C6 | 1.4108 (14) | C14—C15 | 1.4429 (17) |
| N2—C3 | 1.3263 (15) | C14—H14 | 0.9300 |
| C3—C4 | 1.4332 (18) | C15—H15 | 0.9300 |
| C3—C16 | 1.4726 (16) | C16—C17 | 1.386 (2) |
| C4—C5 | 1.3734 (16) | C16—C21 | 1.3896 (17) |
| C4—C23 | 1.449 (2) | C17—C18 | 1.3806 (18) |
| C5—H5 | 0.9300 | C17—H17 | 0.9300 |
| C6—C14 | 1.3364 (18) | C18—C19 | 1.384 (2) |
| C6—C7 | 1.4804 (16) | C18—H18 | 0.9300 |
| C7—C12 | 1.3771 (19) | C19—C20 | 1.373 (2) |
| C7—C8 | 1.3807 (19) | C19—C22 | 1.5072 (17) |
| C8—C9 | 1.382 (2) | C20—C21 | 1.3864 (18) |
| C8—H8 | 0.9300 | C20—H20 | 0.9300 |
| C9—C10 | 1.373 (3) | C21—H21 | 0.9300 |
| C9—H9 | 0.9300 | C22—H22A | 0.9600 |
| C10—C11 | 1.367 (3) | C22—H22B | 0.9600 |
| C10—C13 | 1.507 (2) | C22—H22C | 0.9600 |
| C11—C12 | 1.393 (2) | C23—H23 | 0.9300 |
| C11—H11 | 0.9300 | | |

| | | | |
|---|---|---|---|
| C5—N1—N2 | 111.71 (9) | C10—C13—H13C | 109.5 |
| C5—N1—C6 | 127.40 (10) | H13A—C13—H13C | 109.5 |
| N2—N1—C6 | 120.86 (10) | H13B—C13—H13C | 109.5 |
| C3—N2—N1 | 105.69 (10) | C6—C14—C15 | 122.12 (12) |
| N2—C3—C4 | 110.22 (10) | C6—C14—H14 | 118.9 |
| N2—C3—C16 | 117.81 (11) | C15—C14—H14 | 118.9 |
| C4—C3—C16 | 131.96 (11) | O1—C15—C14 | 124.02 (14) |
| C5—C4—C3 | 104.78 (11) | O1—C15—H15 | 118.0 |
| C5—C4—C23 | 119.51 (13) | C14—C15—H15 | 118.0 |
| C3—C4—C23 | 135.70 (12) | C17—C16—C21 | 117.85 (11) |
| N1—C5—C4 | 107.59 (11) | C17—C16—C3 | 119.56 (11) |
| N1—C5—H5 | 126.2 | C21—C16—C3 | 122.58 (12) |
| C4—C5—H5 | 126.2 | C18—C17—C16 | 121.04 (12) |
| C14—C6—N1 | 120.30 (11) | C18—C17—H17 | 119.5 |
| C14—C6—C7 | 125.66 (10) | C16—C17—H17 | 119.5 |
| N1—C6—C7 | 114.03 (10) | C17—C18—C19 | 121.24 (14) |
| C12—C7—C8 | 118.58 (12) | C17—C18—H18 | 119.4 |
| C12—C7—C6 | 121.17 (12) | C19—C18—H18 | 119.4 |
| C8—C7—C6 | 120.25 (11) | C20—C19—C18 | 117.67 (12) |

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| C7—C8—C9 | 120.59 (14) | C20—C19—C22 | 121.35 (13) |
| C7—C8—H8 | 119.7 | C18—C19—C22 | 120.99 (14) |
| C9—C8—H8 | 119.7 | C19—C20—C21 | 121.80 (12) |
| C10—C9—C8 | 121.24 (15) | C19—C20—H20 | 119.1 |
| C10—C9—H9 | 119.4 | C21—C20—H20 | 119.1 |
| C8—C9—H9 | 119.4 | C20—C21—C16 | 120.39 (14) |
| C11—C10—C9 | 118.04 (14) | C20—C21—H21 | 119.8 |
| C11—C10—C13 | 121.26 (18) | C16—C21—H21 | 119.8 |
| C9—C10—C13 | 120.70 (19) | C19—C22—H22A | 109.5 |
| C10—C11—C12 | 121.64 (15) | C19—C22—H22B | 109.5 |
| C10—C11—H11 | 119.2 | H22A—C22—H22B | 109.5 |
| C12—C11—H11 | 119.2 | C19—C22—H22C | 109.5 |
| C7—C12—C11 | 119.90 (15) | H22A—C22—H22C | 109.5 |
| C7—C12—H12 | 120.1 | H22B—C22—H22C | 109.5 |
| C11—C12—H12 | 120.1 | O2—C23—C4 | 127.49 (16) |
| C10—C13—H13A | 109.5 | O2—C23—H23 | 116.3 |
| C10—C13—H13B | 109.5 | C4—C23—H23 | 116.3 |
| H13A—C13—H13B | 109.5 | | |

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| C5—N1—N2—C3 | −1.10 (14) | C9—C10—C11—C12 | 0.4 (2) |
| C6—N1—N2—C3 | −178.96 (11) | C13—C10—C11—C12 | −178.80 (16) |
| N1—N2—C3—C4 | 1.07 (14) | C8—C7—C12—C11 | −1.4 (2) |
| N1—N2—C3—C16 | −178.26 (10) | C6—C7—C12—C11 | 177.74 (13) |
| N2—C3—C4—C5 | −0.68 (15) | C10—C11—C12—C7 | 1.0 (3) |
| C16—C3—C4—C5 | 178.52 (13) | N1—C6—C14—C15 | −175.47 (12) |
| N2—C3—C4—C23 | −179.31 (18) | C7—C6—C14—C15 | 3.5 (2) |
| C16—C3—C4—C23 | −0.1 (3) | C6—C14—C15—O1 | −175.65 (15) |
| N2—N1—C5—C4 | 0.69 (15) | N2—C3—C16—C17 | 16.27 (18) |
| C6—N1—C5—C4 | 178.37 (12) | C4—C3—C16—C17 | −162.88 (14) |
| C3—C4—C5—N1 | −0.02 (15) | N2—C3—C16—C21 | −162.11 (13) |
| C23—C4—C5—N1 | 178.89 (14) | C4—C3—C16—C21 | 18.7 (2) |
| C5—N1—C6—C14 | −163.17 (14) | C21—C16—C17—C18 | 0.7 (2) |
| N2—N1—C6—C14 | 14.31 (18) | C3—C16—C17—C18 | −177.75 (13) |
| C5—N1—C6—C7 | 17.72 (18) | C16—C17—C18—C19 | −0.2 (2) |
| N2—N1—C6—C7 | −164.79 (11) | C17—C18—C19—C20 | −0.7 (2) |
| C14—C6—C7—C12 | 72.91 (19) | C17—C18—C19—C22 | 178.93 (14) |
| N1—C6—C7—C12 | −108.04 (14) | C18—C19—C20—C21 | 0.9 (2) |
| C14—C6—C7—C8 | −107.93 (16) | C22—C19—C20—C21 | −178.68 (13) |
| N1—C6—C7—C8 | 71.12 (15) | C19—C20—C21—C16 | −0.4 (2) |
| C12—C7—C8—C9 | 0.5 (2) | C17—C16—C21—C20 | −0.5 (2) |
| C6—C7—C8—C9 | −178.73 (13) | C3—C16—C21—C20 | 177.95 (12) |
| C7—C8—C9—C10 | 1.0 (2) | C5—C4—C23—O2 | −175.2 (2) |
| C8—C9—C10—C11 | −1.4 (2) | C3—C4—C23—O2 | 3.3 (4) |
| C8—C9—C10—C13 | 177.79 (15) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C22—H22*A*···O2$^{i}$ | 0.96 | 2.60 | 3.378 (2) | 139 |
| C5—H5···O1$^{ii}$ | 0.93 | 2.23 | 3.1094 (17) | 159 |

Symmetry codes: (i) −*x*+3, −*y*, −*z*; (ii) −*x*+3/2, *y*−1/2, −*z*+1/2.