

# Crystal structure of ethyl 2-[2-(4-methylbenzoyl)-5-*p*-tolyl-1*H*-imidazol-1-yl]acetate

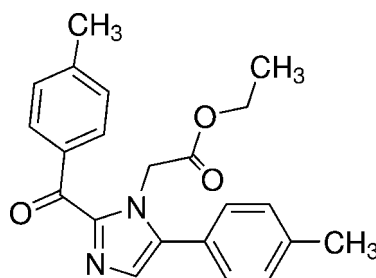
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In the title compound, C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>, the plane of the five-membered ring is oriented at dihedral angles of 45.4 (1) and 52.5 (1)° to the phenyl rings. Furthermore, this ring makes an angle of 85.2 (2)° with the plane of the ethyl acetate substituent. The molecular structure is affected by an intramolecular C—H···O hydrogen bond between an H atom from the *p*-tolyl group and the carbonyl O atom of the acetate. The methyl group of the ethyl acetate residue is disordered over two sites with equal occupancies. The crystal structure features intermolecular C—H···O and C—H···N interactions. One of the C—H···O hydrogen bonds forms a C(5) chain motif extending along the *a* axis. In addition, C—H···N contacts form inversion dimers with R<sub>2</sub><sup>2</sup>(12) ring motifs, linking the imidazole ring system to the benzene ring of the *p*-tolyl substituent.

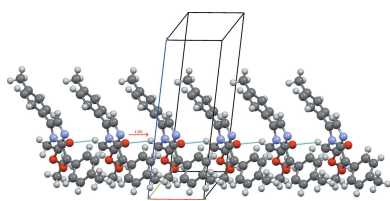
## 1. Chemical context

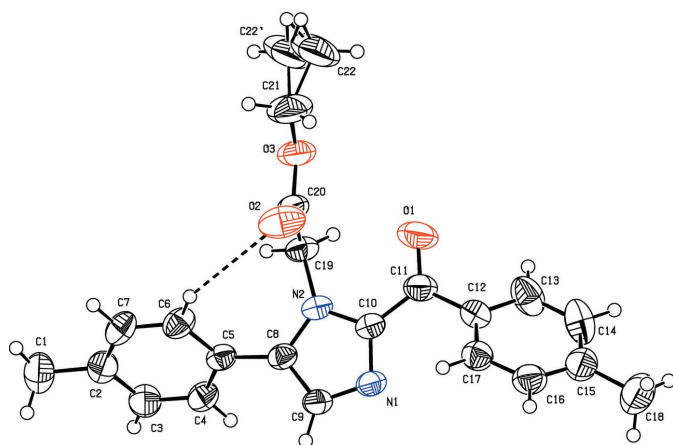
Imidazole and its derivatives have numerous pharmaceutical applications including uses as antifungal (Shingalapur *et al.* 2009), antimicrobial (Sharma *et al.* 2009), anti-inflammatory (Puratchikody *et al.* 2007), analgesic (Achar *et al.* 2010), antitubercular (Pandey *et al.* 2009), antidepressant (Hadi-zadeh *et al.* 2008), antileishmanial (Bhandari *et al.* 2009) and anticancer agents (Ozkay *et al.* 2010). We are interested in the synthesis of active pharmaceutical ingredients (APIs) based on imidazoles and we report here the synthesis and crystal structure of the title imidazole derivative.



## 2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The C—N bond lengths within the imidazole ring are 1.373 (3) Å (C10—N2), 1.372 (3) Å (C8—N2), 1.349 (3) Å (C9—N1) and 1.329 (3) Å (C10—N1). These bond distances



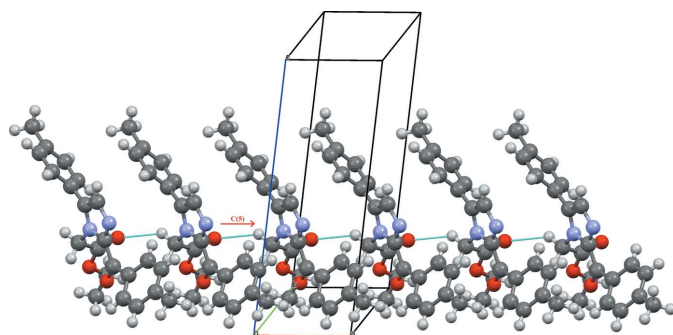

**Figure 1**

The molecular structure of the title compound, showing the atom-numbering scheme and 50% probability displacement ellipsoids. The methyl group (C22) of the side chain is disordered over two positions each with 0.5 occupancy.

are shorter than the single-bond length (1.443 Å) and longer than the accepted double-bond length (1.269 Å) due to electron delocalization in the central imidazole ring. The phenyl rings and the plane of the imidazole ring are inclined at angles of 45.4 (1)° (with the C12–C17 ring) and 52.5 (1)° (with the C2–C7 ring). The phenyl rings are oriented to each other with a dihedral angle of 88.1 (1)°. Further, the imidazole ring is inclined at an angle of 85.2 (2)° to the best-fit plane through atoms C19, C20, O3, C21 and C22 of the ethyl acetate substituent. The molecular structure is also influenced by the formation of an intramolecular C6–H6···O2 hydrogen bond, Table 1, which generates an *S*(8) ring motif (Bernstein *et al.*, 1995).

### 3. Supramolecular features

The N-bound methylene group of the side chain is connected with the carbonyl oxygen of an adjacent molecule through a C19–H19A···O2 hydrogen bond, forming a linear *C*(5) chain motif along the *a* axis, Table 1 and Fig. 2. The phenyl and


**Figure 2**

Linear *C*(5) chains formed by a C–H···O intermolecular interaction extending along the *a* axis of the unit cell.

**Table 1**

Hydrogen-bond geometry (Å, °).

| <i>D</i> –H··· <i>A</i>      | <i>D</i> –H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> –H··· <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| C6–H6···O2                   | 0.93        | 2.91          | 3.723 (4)             | 147                     |
| C1–H1A···O2 <sup>i</sup>     | 0.96        | 2.71          | 3.605 (4)             | 155                     |
| C4–H4···N1 <sup>ii</sup>     | 0.93        | 2.83          | 3.724 (3)             | 161                     |
| C19–H19A···O2 <sup>iii</sup> | 0.97        | 2.51          | 3.309 (3)             | 140                     |

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

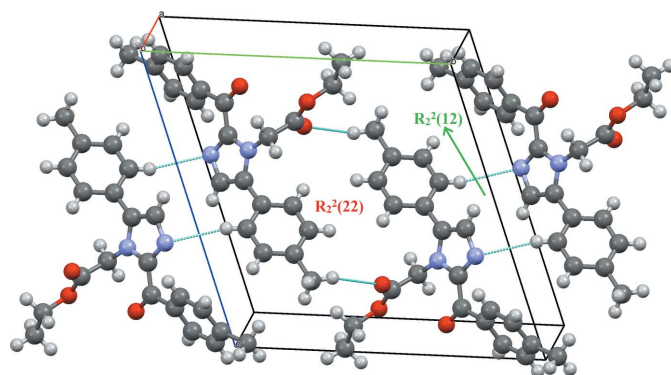
imidazole rings are linked through inversion-dimer formation involving C4–H4···N1 hydrogen bonds that generate  $R_2^2(12)$  ring motifs. A second inversion dimer to an adjacent molecule results from C1–H1···O2 contacts, forming ring  $R_2^2(22)$  [OK?] rings, Fig. 3.

### 4. Database survey

The Cambridge Structural Database (Groom & Allen, 2014) reveals only five structures of imidazole derivatives with a CH<sub>2</sub>COOCH<sub>2</sub>CH<sub>3</sub> substituent on nitrogen (Cai *et al.*, 2014; Bahnous *et al.*, 2013; Zaprutko *et al.*, 2012). Imidazoles with benzoyl substituents are slightly more common with eight occurrences (Xue *et al.*, 2014; Nagaraj *et al.*, 2012; Samanta *et al.*, 2013), while the structures of only six *p*-tolyl-substituted imidazoles are found (Bu *et al.*, 1996; Fridman *et al.*, 2006, 2009). These searches also reveal the unique nature of the molecule reported here.

### 5. Synthesis and crystallization

The title compound was synthesized from a mixture of 2-(4-methoxyphenyl)-2-oxoacetaldehyde (1 mmol), glycine methyl ester hydrochloride (1 mmol) and selenium dioxide (1 mmol) in a basic environment in acetonitrile at 373 K. Crystals suitable for X-ray investigation were obtained by solvent evaporation from the resulting solution in 33% yield.


**Figure 3**

Inversion dimers with  $R_2^2(12)$  and  $R_2^2(22)$  ring motifs resulting from C–H···N and C–H···O hydrogen bonds.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93–0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{parent C atom})$ . The methyl group C22 of the side chain is disordered over two positions, each with a site-occupancy factor of 0.5. The atomic displacement parameters of these two C atoms are restrained to be equivalent and the C21–C22 and C21–C22' bond distances were restrained during the refinement using DFIX commands.

## Acknowledgements

SA and SSK thank the Department of Science and Technology, New Delhi, for financial support of this work through the Fasttrack Young Scientist scheme.

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Table 2

Experimental details.

|  |   |
|--|---|
| Crystal data   |   |
| Chemical formula   | C <sub>22</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> |
| $M_r$  | 362.41  |
| Crystal system, space group  | Triclinic, $P\bar{1}$   |
| Temperature (K)  | 293   |
| $a, b, c$ (Å)  | 5.0968 (5), 13.8189 (15),<br>14.6993 (17)                     |
| $\alpha, \beta, \gamma$ (°)  | 71.484 (5), 84.018 (5), 82.531 (5)                            |
| $V$ (Å <sup>3</sup> )  | 971.20 (18)   |
| $Z$  | 2   |
| Radiation type   | Mo $K\alpha$  |
| $\mu$ (mm <sup>-1</sup> )  | 0.08  |
| Crystal size (mm)  | 0.21 × 0.19 × 0.16  |
| Data collection  |   |
| Diffractionmeter   | Bruker SMART APEX CCD area-detector                           |
| No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections | 18453, 3405, 2354   |
| $R_{\text{int}}$   | 0.055   |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )                    | 0.595   |
| Refinement   |   |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$  | 0.054, 0.168, 1.07  |
| No. of reflections   | 3405  |
| No. of parameters  | 251   |
| No. of restraints  | 2   |
| H-atom treatment   | H-atom parameters constrained                                 |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )    | 0.52, -0.31   |

Computer programs: *SMART* (Bruker, 2001), *SAINT* (Bruker, 2001), *SHELXTL/PC* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

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## supporting information

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## Crystal structure of ethyl 2-[2-(4-methylbenzoyl)-5-*p*-tolyl-1*H*-imidazol-1-yl]acetate

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### Computing details

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL/PC* (Sheldrick, 2008).

### Ethyl 2-[2-(4-methylbenzoyl)-5-*p*-tolyl-1*H*-imidazol-1-yl]acetate

#### Crystal data

$C_{22}H_{22}N_2O_3$

$M_r = 362.41$

Triclinic,  $P\bar{1}$

$a = 5.0968$  (5) Å

$b = 13.8189$  (15) Å

$c = 14.6993$  (17) Å

$\alpha = 71.484$  (5)°

$\beta = 84.018$  (5)°

$\gamma = 82.531$  (5)°

$V = 971.20$  (18) Å<sup>3</sup>

$Z = 2$

$F(000) = 384$

$D_x = 1.239$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2986 reflections

$\theta = 2.1$ – $24.4$ °

$\mu = 0.08$  mm<sup>-1</sup>

$T = 293$  K

Block, colourless

$0.21 \times 0.19 \times 0.16$  mm

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

$\omega$  scans

18453 measured reflections

3405 independent reflections

2354 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.055$

$\theta_{max} = 25.0$ °,  $\theta_{min} = 2.5$ °

$h = -6$ → $6$

$k = -16$ → $16$

$l = -17$ → $17$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.168$

$S = 1.07$

3405 reflections

251 parameters

2 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.5608P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.52$  e Å<sup>-3</sup>

$\Delta\rho_{min} = -0.30$  e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

|      | <i>x</i>    | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|-------------|--------------|--------------|----------------------------------|-----------|
| C1   | -0.6633 (7) | 0.3819 (3)   | 0.6826 (2)   | 0.0754 (9)                       |           |
| H1A  | -0.6105     | 0.4476       | 0.6779       | 0.113*                           |           |
| H1B  | -0.6498     | 0.3372       | 0.7474       | 0.113*                           |           |
| H1C  | -0.8433     | 0.3901       | 0.6655       | 0.113*                           |           |
| C2   | -0.4852 (5) | 0.3362 (2)   | 0.61545 (19) | 0.0530 (7)                       |           |
| C3   | -0.5093 (5) | 0.2386 (2)   | 0.6123 (2)   | 0.0568 (7)                       |           |
| H3   | -0.6403     | 0.2015       | 0.6517       | 0.068*                           |           |
| C4   | -0.3441 (5) | 0.19537 (19) | 0.55220 (19) | 0.0501 (6)                       |           |
| H4   | -0.3636     | 0.1293       | 0.5524       | 0.060*                           |           |
| C5   | -0.1486 (5) | 0.24912 (17) | 0.49132 (17) | 0.0426 (6)                       |           |
| C6   | -0.1244 (5) | 0.34725 (19) | 0.4938 (2)   | 0.0536 (7)                       |           |
| H6   | 0.0048      | 0.3851       | 0.4539       | 0.064*                           |           |
| C7   | -0.2906 (5) | 0.3891 (2)   | 0.5551 (2)   | 0.0573 (7)                       |           |
| H7   | -0.2705     | 0.4548       | 0.5557       | 0.069*                           |           |
| C8   | 0.0360 (5)  | 0.19884 (17) | 0.43313 (17) | 0.0419 (6)                       |           |
| C9   | 0.1875 (5)  | 0.10614 (18) | 0.46091 (18) | 0.0466 (6)                       |           |
| H9   | 0.1835      | 0.0613       | 0.5233       | 0.056*                           |           |
| C10  | 0.2885 (5)  | 0.16918 (17) | 0.31157 (17) | 0.0428 (6)                       |           |
| C11  | 0.4033 (5)  | 0.1806 (2)   | 0.21394 (19) | 0.0539 (7)                       |           |
| C12  | 0.6016 (5)  | 0.0980 (2)   | 0.19780 (17) | 0.0480 (6)                       |           |
| C17  | 0.8022 (5)  | 0.0507 (2)   | 0.25858 (19) | 0.0514 (7)                       |           |
| H17  | 0.8186      | 0.0717       | 0.3117       | 0.062*                           |           |
| C16  | 0.9772 (6)  | -0.0268 (2)  | 0.2414 (2)   | 0.0614 (8)                       |           |
| H16  | 1.1136      | -0.0560      | 0.2821       | 0.074*                           |           |
| C15  | 0.9556 (6)  | -0.0622 (2)  | 0.1653 (2)   | 0.0629 (8)                       |           |
| C14  | 0.7592 (7)  | -0.0130 (3)  | 0.1034 (2)   | 0.0777 (10)                      |           |
| H14  | 0.7426      | -0.0345      | 0.0505       | 0.093*                           |           |
| C13  | 0.5874 (6)  | 0.0671 (3)   | 0.1182 (2)   | 0.0709 (9)                       |           |
| H13  | 0.4612      | 0.1004       | 0.0742       | 0.085*                           |           |
| C18  | 1.1384 (8)  | -0.1519 (3)  | 0.1513 (3)   | 0.0990 (13)                      |           |
| H18A | 1.0844      | -0.1703      | 0.0988       | 0.149*                           |           |
| H18B | 1.1306      | -0.2092      | 0.2089       | 0.149*                           |           |
| H18C | 1.3167      | -0.1334      | 0.1372       | 0.149*                           |           |
| C19  | -0.0310 (5) | 0.33098 (18) | 0.27136 (18) | 0.0488 (6)                       |           |
| H19A | -0.1902     | 0.3538       | 0.3044       | 0.059*                           |           |
| H19B | -0.0836     | 0.3150       | 0.2167       | 0.059*                           |           |
| C20  | 0.1464 (5)  | 0.41606 (19) | 0.23635 (19) | 0.0510 (7)                       |           |
| C21  | 0.2175 (8)  | 0.5710 (2)   | 0.1156 (2)   | 0.0923 (12)                      |           |
| H21A | 0.4038      | 0.5456       | 0.1198       | 0.111*                           |           |

|      |            |              |              |            |     |
|------|------------|--------------|--------------|------------|-----|
| H21B | 0.1794     | 0.6196       | 0.1517       | 0.111*     |     |
| C22  | 0.161 (3)  | 0.6255 (15)  | 0.0101 (4)   | 0.119 (4)  | 0.5 |
| H22A | 0.2473     | 0.5850       | -0.0289      | 0.179*     | 0.5 |
| H22B | 0.2273     | 0.6915       | -0.0105      | 0.179*     | 0.5 |
| H22C | -0.0267    | 0.6340       | 0.0036       | 0.179*     | 0.5 |
| C22' | 0.047 (3)  | 0.6433 (15)  | 0.0364 (5)   | 0.119 (4)  | 0.5 |
| H22D | 0.0075     | 0.6068       | -0.0055      | 0.179*     | 0.5 |
| H22E | 0.1418     | 0.7005       | 0.0001       | 0.179*     | 0.5 |
| H22F | -0.1156    | 0.6677       | 0.0651       | 0.179*     | 0.5 |
| N1   | 0.3431 (4) | 0.08765 (14) | 0.38698 (14) | 0.0464 (5) |     |
| N2   | 0.1006 (4) | 0.23871 (14) | 0.33651 (14) | 0.0434 (5) |     |
| O1   | 0.3314 (5) | 0.25504 (18) | 0.14648 (15) | 0.0913 (8) |     |
| O2   | 0.3358 (4) | 0.42182 (16) | 0.27496 (17) | 0.0774 (7) |     |
| O3   | 0.0563 (4) | 0.48554 (13) | 0.15783 (13) | 0.0663 (6) |     |

*Atomic displacement parameters (Å<sup>2</sup>)*

|      | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| C1   | 0.077 (2)   | 0.081 (2)   | 0.077 (2)   | 0.0039 (17)  | -0.0022 (17) | -0.0423 (18) |
| C2   | 0.0517 (15) | 0.0546 (16) | 0.0558 (16) | 0.0006 (13)  | -0.0118 (13) | -0.0211 (13) |
| C3   | 0.0558 (16) | 0.0555 (17) | 0.0601 (17) | -0.0134 (13) | 0.0026 (13)  | -0.0185 (14) |
| C4   | 0.0553 (15) | 0.0386 (13) | 0.0585 (16) | -0.0095 (12) | -0.0050 (13) | -0.0155 (12) |
| C5   | 0.0453 (13) | 0.0361 (12) | 0.0458 (14) | -0.0031 (10) | -0.0120 (11) | -0.0094 (11) |
| C6   | 0.0531 (15) | 0.0392 (14) | 0.0681 (18) | -0.0111 (12) | -0.0003 (13) | -0.0149 (13) |
| C7   | 0.0617 (17) | 0.0408 (14) | 0.0759 (19) | -0.0036 (13) | -0.0105 (15) | -0.0259 (14) |
| C8   | 0.0475 (14) | 0.0331 (12) | 0.0450 (14) | -0.0075 (10) | -0.0073 (11) | -0.0092 (11) |
| C9   | 0.0595 (16) | 0.0362 (13) | 0.0405 (14) | -0.0052 (11) | -0.0059 (12) | -0.0060 (11) |
| C10  | 0.0459 (14) | 0.0346 (12) | 0.0447 (14) | -0.0027 (10) | -0.0072 (11) | -0.0071 (11) |
| C11  | 0.0557 (16) | 0.0496 (15) | 0.0467 (15) | -0.0009 (12) | -0.0049 (12) | -0.0025 (12) |
| C12  | 0.0499 (15) | 0.0515 (15) | 0.0401 (14) | -0.0078 (12) | -0.0016 (11) | -0.0099 (11) |
| C17  | 0.0535 (15) | 0.0524 (15) | 0.0478 (15) | -0.0058 (13) | -0.0060 (12) | -0.0136 (12) |
| C16  | 0.0600 (17) | 0.0582 (17) | 0.0561 (17) | 0.0031 (14)  | -0.0026 (13) | -0.0077 (14) |
| C15  | 0.0662 (19) | 0.0526 (17) | 0.0669 (19) | -0.0124 (14) | 0.0146 (15)  | -0.0175 (15) |
| C14  | 0.074 (2)   | 0.109 (3)   | 0.070 (2)   | -0.016 (2)   | 0.0051 (17)  | -0.055 (2)   |
| C13  | 0.0578 (18) | 0.106 (3)   | 0.0529 (17) | 0.0029 (17)  | -0.0105 (14) | -0.0325 (17) |
| C18  | 0.116 (3)   | 0.063 (2)   | 0.112 (3)   | -0.003 (2)   | 0.032 (2)    | -0.032 (2)   |
| C19  | 0.0471 (14) | 0.0397 (13) | 0.0500 (15) | 0.0019 (11)  | -0.0091 (11) | -0.0010 (11) |
| C20  | 0.0540 (16) | 0.0381 (14) | 0.0522 (15) | 0.0030 (12)  | -0.0057 (13) | -0.0041 (12) |
| C21  | 0.133 (3)   | 0.0462 (18) | 0.085 (2)   | -0.0256 (19) | -0.012 (2)   | 0.0059 (17)  |
| C22  | 0.199 (13)  | 0.099 (7)   | 0.050 (4)   | -0.063 (7)   | 0.004 (6)    | 0.004 (6)    |
| C22' | 0.199 (13)  | 0.099 (7)   | 0.050 (4)   | -0.063 (7)   | 0.004 (6)    | 0.004 (6)    |
| N1   | 0.0566 (13) | 0.0345 (11) | 0.0443 (12) | -0.0018 (9)  | -0.0086 (10) | -0.0061 (9)  |
| N2   | 0.0462 (11) | 0.0331 (10) | 0.0448 (12) | -0.0018 (9)  | -0.0081 (9)  | -0.0029 (9)  |
| O1   | 0.1031 (18) | 0.0828 (16) | 0.0517 (12) | 0.0282 (14)  | 0.0041 (12)  | 0.0128 (11)  |
| O2   | 0.0675 (13) | 0.0612 (13) | 0.0934 (16) | -0.0175 (11) | -0.0261 (12) | 0.0010 (11)  |
| O3   | 0.0886 (14) | 0.0412 (10) | 0.0577 (12) | -0.0074 (10) | -0.0135 (10) | 0.0037 (9)   |

*Geometric parameters (Å, °)*

|            |           |               |           |
|------------|-----------|---------------|-----------|
| C1—C2      | 1.503 (4) | C16—C15       | 1.375 (4) |
| C1—H1A     | 0.9600    | C16—H16       | 0.9300    |
| C1—H1B     | 0.9600    | C15—C14       | 1.383 (4) |
| C1—H1C     | 0.9600    | C15—C18       | 1.506 (4) |
| C2—C7      | 1.377 (4) | C14—C13       | 1.379 (4) |
| C2—C3      | 1.386 (4) | C14—H14       | 0.9300    |
| C3—C4      | 1.377 (4) | C13—H13       | 0.9300    |
| C3—H3      | 0.9300    | C18—H18A      | 0.9600    |
| C4—C5      | 1.389 (3) | C18—H18B      | 0.9600    |
| C4—H4      | 0.9300    | C18—H18C      | 0.9600    |
| C5—C6      | 1.390 (3) | C19—N2        | 1.459 (3) |
| C5—C8      | 1.463 (3) | C19—C20       | 1.503 (4) |
| C6—C7      | 1.381 (4) | C19—H19A      | 0.9700    |
| C6—H6      | 0.9300    | C19—H19B      | 0.9700    |
| C7—H7      | 0.9300    | C20—O2        | 1.193 (3) |
| C8—C9      | 1.371 (3) | C20—O3        | 1.325 (3) |
| C8—N2      | 1.372 (3) | C21—O3        | 1.462 (4) |
| C9—N1      | 1.349 (3) | C21—C22       | 1.534 (2) |
| C9—H9      | 0.9300    | C21—C22'      | 1.535 (2) |
| C10—N1     | 1.329 (3) | C21—H21A      | 0.9700    |
| C10—N2     | 1.373 (3) | C21—H21B      | 0.9700    |
| C10—C11    | 1.460 (4) | C22—H22A      | 0.9600    |
| C11—O1     | 1.227 (3) | C22—H22B      | 0.9600    |
| C11—C12    | 1.484 (4) | C22—H22C      | 0.9600    |
| C12—C13    | 1.379 (4) | C22'—H22D     | 0.9600    |
| C12—C17    | 1.384 (3) | C22'—H22E     | 0.9600    |
| C17—C16    | 1.373 (4) | C22'—H22F     | 0.9600    |
| C17—H17    | 0.9300    |               |           |
|            |           |               |           |
| C2—C1—H1A  | 109.5     | C14—C15—C18   | 121.8 (3) |
| C2—C1—H1B  | 109.5     | C13—C14—C15   | 121.5 (3) |
| H1A—C1—H1B | 109.5     | C13—C14—H14   | 119.2     |
| C2—C1—H1C  | 109.5     | C15—C14—H14   | 119.2     |
| H1A—C1—H1C | 109.5     | C12—C13—C14   | 120.4 (3) |
| H1B—C1—H1C | 109.5     | C12—C13—H13   | 119.8     |
| C7—C2—C3   | 117.3 (3) | C14—C13—H13   | 119.8     |
| C7—C2—C1   | 121.5 (3) | C15—C18—H18A  | 109.5     |
| C3—C2—C1   | 121.2 (3) | C15—C18—H18B  | 109.5     |
| C4—C3—C2   | 121.6 (3) | H18A—C18—H18B | 109.5     |
| C4—C3—H3   | 119.2     | C15—C18—H18C  | 109.5     |
| C2—C3—H3   | 119.2     | H18A—C18—H18C | 109.5     |
| C3—C4—C5   | 120.8 (2) | H18B—C18—H18C | 109.5     |
| C3—C4—H4   | 119.6     | N2—C19—C20    | 111.7 (2) |
| C5—C4—H4   | 119.6     | N2—C19—H19A   | 109.3     |
| C4—C5—C6   | 117.8 (2) | C20—C19—H19A  | 109.3     |
| C4—C5—C8   | 119.7 (2) | N2—C19—H19B   | 109.3     |



|               |            |                 |             |
|---------------|------------|-----------------|-------------|
| C6—C5—C8      | 122.3 (2)  | C20—C19—H19B    | 109.3       |
| C7—C6—C5      | 120.5 (2)  | H19A—C19—H19B   | 107.9       |
| C7—C6—H6      | 119.7      | O2—C20—O3       | 124.9 (2)   |
| C5—C6—H6      | 119.7      | O2—C20—C19      | 125.1 (2)   |
| C2—C7—C6      | 121.9 (2)  | O3—C20—C19      | 109.9 (2)   |
| C2—C7—H7      | 119.1      | O3—C21—C22      | 111.1 (9)   |
| C6—C7—H7      | 119.1      | O3—C21—C22'     | 102.4 (9)   |
| C9—C8—N2      | 104.8 (2)  | O3—C21—H21A     | 109.4       |
| C9—C8—C5      | 129.3 (2)  | C22—C21—H21A    | 109.4       |
| N2—C8—C5      | 125.8 (2)  | O3—C21—H21B     | 109.4       |
| N1—C9—C8      | 112.0 (2)  | C22—C21—H21B    | 109.4       |
| N1—C9—H9      | 124.0      | H21A—C21—H21B   | 108.0       |
| C8—C9—H9      | 124.0      | C21—C22—H22A    | 109.5       |
| N1—C10—N2     | 111.2 (2)  | C21—C22—H22B    | 109.5       |
| N1—C10—C11    | 124.2 (2)  | H22A—C22—H22B   | 109.5       |
| N2—C10—C11    | 124.5 (2)  | C21—C22—H22C    | 109.5       |
| O1—C11—C10    | 120.8 (2)  | H22A—C22—H22C   | 109.5       |
| O1—C11—C12    | 120.8 (2)  | H22B—C22—H22C   | 109.5       |
| C10—C11—C12   | 118.3 (2)  | C21—C22'—H22D   | 109.5       |
| C13—C12—C17   | 118.2 (3)  | C21—C22'—H22E   | 109.5       |
| C13—C12—C11   | 118.7 (2)  | H22D—C22'—H22E  | 109.5       |
| C17—C12—C11   | 123.2 (2)  | C21—C22'—H22F   | 109.5       |
| C16—C17—C12   | 120.8 (3)  | H22D—C22'—H22F  | 109.5       |
| C16—C17—H17   | 119.6      | H22E—C22'—H22F  | 109.5       |
| C12—C17—H17   | 119.6      | C10—N1—C9       | 105.0 (2)   |
| C17—C16—C15   | 121.5 (3)  | C8—N2—C10       | 106.94 (18) |
| C17—C16—H16   | 119.2      | C8—N2—C19       | 125.8 (2)   |
| C15—C16—H16   | 119.2      | C10—N2—C19      | 126.8 (2)   |
| C16—C15—C14   | 117.4 (3)  | C20—O3—C21      | 114.8 (2)   |
| C16—C15—C18   | 120.8 (3)  |                 |             |
| C7—C2—C3—C4   | 0.7 (4)    | C17—C16—C15—C14 | 3.4 (4)     |
| C1—C2—C3—C4   | -178.8 (3) | C17—C16—C15—C18 | -176.0 (3)  |
| C2—C3—C4—C5   | -0.9 (4)   | C16—C15—C14—C13 | -1.4 (5)    |
| C3—C4—C5—C6   | 0.6 (4)    | C18—C15—C14—C13 | 178.0 (3)   |
| C3—C4—C5—C8   | 175.8 (2)  | C17—C12—C13—C14 | 3.8 (4)     |
| C4—C5—C6—C7   | 0.0 (4)    | C11—C12—C13—C14 | -176.6 (3)  |
| C8—C5—C6—C7   | -175.1 (2) | C15—C14—C13—C12 | -2.3 (5)    |
| C3—C2—C7—C6   | -0.2 (4)   | N2—C19—C20—O2   | -20.6 (4)   |
| C1—C2—C7—C6   | 179.4 (3)  | N2—C19—C20—O3   | 161.4 (2)   |
| C5—C6—C7—C2   | -0.2 (4)   | N2—C10—N1—C9    | -0.2 (3)    |
| C4—C5—C8—C9   | -51.0 (4)  | C11—C10—N1—C9   | -177.1 (2)  |
| C6—C5—C8—C9   | 124.0 (3)  | C8—C9—N1—C10    | -0.3 (3)    |
| C4—C5—C8—N2   | 131.5 (3)  | C9—C8—N2—C10    | -0.7 (3)    |
| C6—C5—C8—N2   | -53.5 (4)  | C5—C8—N2—C10    | 177.3 (2)   |
| N2—C8—C9—N1   | 0.7 (3)    | C9—C8—N2—C19    | 172.2 (2)   |
| C5—C8—C9—N1   | -177.2 (2) | C5—C8—N2—C19    | -9.8 (4)    |
| N1—C10—C11—O1 | 175.3 (3)  | N1—C10—N2—C8    | 0.6 (3)     |



|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| N2—C10—C11—O1   | -1.2 (4)   | C11—C10—N2—C8   | 177.5 (2)  |
| N1—C10—C11—C12  | -2.5 (4)   | N1—C10—N2—C19   | -172.3 (2) |
| N2—C10—C11—C12  | -179.0 (2) | C11—C10—N2—C19  | 4.7 (4)    |
| O1—C11—C12—C13  | -39.9 (4)  | C20—C19—N2—C8   | 111.7 (3)  |
| C10—C11—C12—C13 | 137.9 (3)  | C20—C19—N2—C10  | -76.8 (3)  |
| O1—C11—C12—C17  | 139.7 (3)  | O2—C20—O3—C21   | 3.5 (4)    |
| C10—C11—C12—C17 | -42.6 (4)  | C19—C20—O3—C21  | -178.5 (2) |
| C13—C12—C17—C16 | -1.8 (4)   | C22—C21—O3—C20  | 160.0 (6)  |
| C11—C12—C17—C16 | 178.6 (2)  | C22'—C21—O3—C20 | -172.9 (6) |
| C12—C17—C16—C15 | -1.9 (4)   |                 |            |

*Hydrogen-bond geometry (Å, °)*

| <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> |
|-------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C6—H6 $\cdots$ O2                   | 0.93        | 2.91                | 3.723 (4)                  | 147                           |
| C1—H1A $\cdots$ O2 <sup>i</sup>     | 0.96        | 2.71                | 3.605 (4)                  | 155                           |
| C4—H4 $\cdots$ N1 <sup>ii</sup>     | 0.93        | 2.83                | 3.724 (3)                  | 161                           |
| C19—H19A $\cdots$ O2 <sup>iii</sup> | 0.97        | 2.51                | 3.309 (3)                  | 140                           |

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