

# Crystal structure of 2,4-bis(2-chlorophenyl)-7-*tert*-pentyl-3-azabicyclo[3.3.1]nonan-9-one

Dong Ho Park,<sup>a</sup> V. Ramkumar<sup>b</sup> and P. Parthiban<sup>a,c,\*</sup>

<sup>a</sup>Department of Biomedical Chemistry, Inje University, Gimhae, Gyeongnam 621 749, Republic of Korea, <sup>b</sup>Department of Chemistry, IIT Madras, Chennai 600 036, TamilNadu, India, and <sup>c</sup>Department of Chemistry, VEL TECH, Avadi, Chennai 600 062, India. \*Correspondence e-mail: parthisivam@yahoo.co.in

Received 31 August 2014; accepted 2 October 2014

Edited by V. V. Chernyshev, Moscow State University, Russia

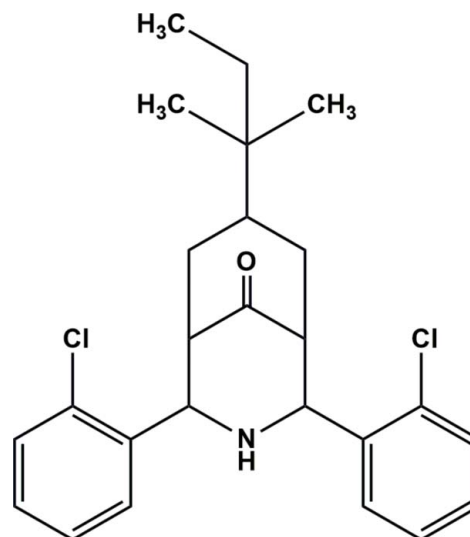
The title compound, C<sub>25</sub>H<sub>29</sub>Cl<sub>2</sub>NO, which is a chloro analog of 2,4-bis(2-bromophenyl)-7-(*tert*-pentyl)-3-azabicyclo[3.3.1]nonan-9-one [Park, Ramkumar & Parthiban (2012). *Acta Cryst. E* **68**, o2946], exists in a twin-chair conformation with an equatorial orientation of the 2-chlorophenyl groups. The *tert*-pentyl group on the cyclohexanone adopts an exocyclic equatorial position and is disordered between two orientations in a ratio 0.520 (8):0.480 (8). The crystal packing shows no directional contacts beyond van der Waals contacts.

**Keywords:** crystal structure; twin-chair conformation; Mannich base; azabicyclo.

**CCDC reference:** 1027325

## 1. Related literature

For the synthesis, stereochemistry and biological activity of 3-azabicyclo[3.3.1]nonan-9-ones, see: Park *et al.* (2011, 2012*a*). For a related crystal structure, see: Park *et al.* (2012*b*). For the conformation of functionalized 3-azabicycles, see: Parthiban *et al.* (2010); Park *et al.* (2012*c*); Padegimas & Kovacic (1972).



## 2. Experimental

### 2.1. Crystal data

|  |   |
|--|---|
| C <sub>25</sub> H <sub>29</sub> Cl <sub>2</sub> NO | $\gamma = 98.266 (2)^\circ$               |
| $M_r = 430.39$                                     | $V = 1130.54 (9) \text{ \AA}^3$           |
| Triclinic, $P\bar{1}$                              | $Z = 2$                                   |
| $a = 7.6006 (3) \text{ \AA}$                       | Mo $K\alpha$ radiation                    |
| $b = 10.6240 (5) \text{ \AA}$                      | $\mu = 0.30 \text{ mm}^{-1}$              |
| $c = 15.1124 (7) \text{ \AA}$                      | $T = 298 \text{ K}$                       |
| $\alpha = 106.116 (2)^\circ$                       | $0.25 \times 0.20 \times 0.15 \text{ mm}$ |
| $\beta = 99.996 (2)^\circ$                         |   |

### 2.2. Data collection

|  |  |
|--|--|
| Bruker APEXII area-detector diffractometer               | 13160 measured reflections             |
| Absorption correction: multi-scan (SADABS; Bruker, 2004) | 3789 independent reflections           |
| $T_{\min} = 0.928$ , $T_{\max} = 0.955$                  | 2944 reflections with $I > 2\sigma(I)$ |
|  | $R_{\text{int}} = 0.020$               |

### 2.3. Refinement

|                                 |  |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.119$               | $\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$                    |
| $S = 1.03$                      | $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$                   |
| 3789 reflections                |  |
| 313 parameters                  |  |
| 13 restraints                   |  |

Data collection: APEX2 (Bruker, 2004); cell refinement: APEX2 and SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus and XPREP (Bruker, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: SHELXL2013.

## Acknowledgements

This research was supported by Inje University Research Grant 2014.

---

Supporting information for this paper is available from the IUCr electronic archives (Reference: CV5472).

---

### References

Bruker (2004). *APEX2, XPREP, SAINT-Plus and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.  
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Padegimas, S. J. & Kovacic, P. (1972). *J. Org. Chem.* **37**, 2672–2676.  
Park, D. H., Jeong, Y. T. & Parthiban, P. (2011). *J. Mol. Struct.* **1005**, 31–44.  
Park, D. H., Ramkumar, V. & Parthiban, P. (2012*b*). *Acta Cryst.* **E68**, o2946.  
Park, D. H., Ramkumar, V. & Parthiban, P. (2012*c*). *Acta Cryst.* **E68**, o1481.  
Park, D. H., Venkatesan, J., Kim, S. K. & Parthiban, P. (2012*a*). *Bioorg. Med. Chem. Lett.* **22**, 6004–6009.  
Parthiban, P., Ramkumar, V. & Jeong, Y. T. (2010). *Acta Cryst.* **E66**, o194–o195.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

## supporting information

*Acta Cryst.* (2014). E70, o1161–o1162 [doi:10.1107/S160053681402176X]

## Crystal structure of 2,4-bis(2-chlorophenyl)-7-*tert*-pentyl-3-azabicyclo[3.3.1]nonan-9-one

Dong Ho Park, V. Ramkumar and P. Parthiban

### S1. Comment

Three major conformations, *viz.*, chair-chair (Parthiban *et al.*, 2010), chair-boat (Park *et al.*, 2012*c*), and boat-boat (Padegimas & Kovacic, 1972) are possible for the bicycle. Hence, the present study is to investigate the stereochemistry of the title compound.

The detailed analysis of asymmetry parameters and torsion angles of the title compound reveal that the values are very similar to its bromo analog. The torsion angles of the title compound C5—C6—C8—C2, C3—C2—C8—C6, C7—C6—C8—C2 and C1—C2—C8—C6 are 63.0 (2), -63.0 (2), -62.6 (2) and 62.4 (2)°, respectively. These values indicate the slightly distorted chair conformation for both six-membered cycles of the fused bicycle.

The orientation of the chlorophenyl groups on both sides of the secondary amino group is identified as equatorial by their torsion angles. The torsion angle of C15—C7—C6—C8 and C8—C2—C1—C9 are 179.99 (17) and -179.01 (17)°, respectively. The orientation of *tert*-pentyl group on the cyclohexanone ring is also identified as equatorial by the following torsion angles: C21—C4—C5—C6 and C21—C4—C3—C2 are 172.3 (9) and -172.6 (12)°, respectively [C21A—C4—C5—C6 and C21A—C4—C3—C2 are 173.7 (10) and -172.9 (11)°, respectively].

The chloro substituted benzene rings of the title compound is oriented very similar to that of its bromo analog. The benzene rings are inclined to each other with an angle of 29.38°, where as the orientation of bromo analog is 29.6 (3)°.

Based on the complete crystallographic analysis, it is concluded that the title compound, C<sub>25</sub>H<sub>29</sub>Cl<sub>2</sub>NO, exists in a twin-chair conformation with an equatorial orientation of the 2-chlorophenyl groups.

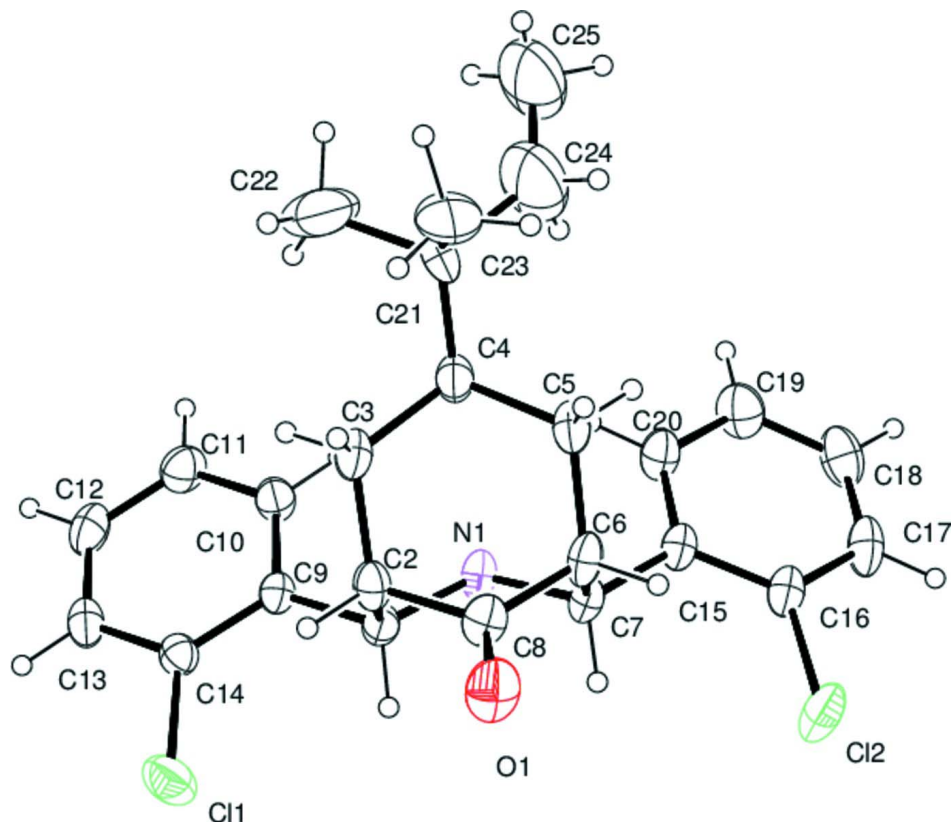
### S2. Experimental

2,4-Bis(2-chlorophenyl)-7-(*tert*-pentyl)-3-azabicyclo[3.3.1]nonan-9-one was synthesized by a modified and an optimized Mannich condensation in one-pot, using 2-chlorobenzaldehyde (0.1 mol, 14.06 g/11.25 ml), 4-*tert*-pentylcyclohexanone (0.05 mol, 8.41 g/9.15 ml) and ammonium acetate (0.075 mol, 5.78 g) in a 50 ml of absolute ethanol (Park *et al.*, 2011). The mixture was gently warmed on a hot plate at 303–308 K (30–35° C) with moderate stirring till the complete consumption of the starting materials, which was monitored by TLC. At the end, the crude azabicyclic ketone was separated by filtration and gently washed with 1:5 cold ethanol-ether mixture. X-ray diffraction quality crystals of the title compound were obtained by slow evaporation from ethanol.

### S3. Refinement

All hydrogen atoms were fixed geometrically and allowed to ride on the parent carbon atoms with aromatic C—H = 0.93 Å, aliphatic C—H = 0.98 Å, methylene C—H = 0.97 Å. The displacement parameters were set for phenyl, methylene and aliphatic H atoms at  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , methyl H atoms at  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  and the hydrogen atoms were fixed geometrically and allowed to ride on the parent nitrogen atom with N—H = 0.86 Å and the displacement parameter was

set at  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ . The *tert*-pentyl group attached to the carbon atom (C4) is disordered in two orientations in a ratio 0.520 (8):0.480 (8).



**Figure 1**

View of the title molecule showing the atomic numbering and 30% probability displacement ellipsoids. For clarity, only major component of the disordered group is shown.

### 2,4-Bis(2-chlorophenyl)-7-*tert*-pentyl-3-azabicyclo[3.3.1]nonan-9-one

#### Crystal data

$\text{C}_{25}\text{H}_{29}\text{Cl}_2\text{NO}$

$M_r = 430.39$

Triclinic,  $P\bar{1}$

$a = 7.6006 (3) \text{ \AA}$

$b = 10.6240 (5) \text{ \AA}$

$c = 15.1124 (7) \text{ \AA}$

$\alpha = 106.116 (2)^\circ$

$\beta = 99.996 (2)^\circ$

$\gamma = 98.266 (2)^\circ$

$V = 1130.54 (9) \text{ \AA}^3$

$Z = 2$

$F(000) = 456$

$D_x = 1.264 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

$\mu = 0.30 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Block, colourless

$0.25 \times 0.20 \times 0.15 \text{ mm}$

#### Data collection

Bruker APEXII area-detector  
diffractometer

phi and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2004)

$T_{\text{min}} = 0.928$ ,  $T_{\text{max}} = 0.955$

13160 measured reflections

3789 independent reflections

2944 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 2.0^\circ$   
 $h = -9 \rightarrow 6$

$k = -12 \rightarrow 12$   
 $l = -17 \rightarrow 17$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.119$   
 $S = 1.02$   
 3789 reflections  
 313 parameters  
 13 restraints

Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.5471P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.041$   
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

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

|     | x          | y            | z            | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|------------|--------------|--------------|----------------------------------|-----------|
| C1  | 0.3313 (3) | 0.57407 (19) | 0.12669 (15) | 0.0406 (5)                       |           |
| H1  | 0.2254     | 0.5266       | 0.0749       | 0.049*                           |           |
| C2  | 0.2630 (3) | 0.6552 (2)   | 0.21189 (16) | 0.0442 (5)                       |           |
| H2  | 0.1886     | 0.7138       | 0.1906       | 0.053*                           |           |
| C3  | 0.4123 (3) | 0.7409 (2)   | 0.29862 (15) | 0.0468 (5)                       |           |
| H3A | 0.4952     | 0.8002       | 0.2787       | 0.056*                           |           |
| H3B | 0.3556     | 0.7964       | 0.3432       | 0.056*                           |           |
| C4  | 0.5240 (3) | 0.6624 (2)   | 0.35002 (16) | 0.0466 (5)                       |           |
| H4  | 0.6008     | 0.6236       | 0.3083       | 0.056*                           |           |
| C5  | 0.3990 (3) | 0.5446 (2)   | 0.36240 (16) | 0.0486 (6)                       |           |
| H5A | 0.3413     | 0.5789       | 0.4140       | 0.058*                           |           |
| H5B | 0.4737     | 0.4851       | 0.3804       | 0.058*                           |           |
| C6  | 0.2491 (3) | 0.4627 (2)   | 0.27445 (16) | 0.0471 (5)                       |           |
| H6  | 0.1661     | 0.3997       | 0.2925       | 0.057*                           |           |
| C7  | 0.3167 (3) | 0.38288 (19) | 0.18868 (15) | 0.0428 (5)                       |           |
| H7  | 0.2097     | 0.3330       | 0.1382       | 0.051*                           |           |
| C8  | 0.1434 (3) | 0.5563 (2)   | 0.24180 (16) | 0.0488 (6)                       |           |
| C9  | 0.4562 (3) | 0.66577 (19) | 0.09259 (14) | 0.0380 (5)                       |           |
| C10 | 0.6447 (3) | 0.6856 (2)   | 0.12042 (16) | 0.0465 (5)                       |           |
| H10 | 0.6951     | 0.6381       | 0.1580       | 0.056*                           |           |
| C11 | 0.7590 (3) | 0.7744 (2)   | 0.09362 (18) | 0.0562 (6)                       |           |
| H11 | 0.8847     | 0.7862       | 0.1138       | 0.067*                           |           |
| C12 | 0.6891 (4) | 0.8452 (2)   | 0.03757 (17) | 0.0573 (6)                       |           |
| H12 | 0.7669     | 0.9052       | 0.0201       | 0.069*                           |           |
| C13 | 0.5037 (3) | 0.8269 (2)   | 0.00741 (15) | 0.0494 (6)                       |           |
| H13 | 0.4550     | 0.8737       | -0.0312      | 0.059*                           |           |
| C14 | 0.3896 (3) | 0.7384 (2)   | 0.03483 (14) | 0.0419 (5)                       |           |
| C15 | 0.4261 (3) | 0.28405 (19) | 0.21254 (15) | 0.0425 (5)                       |           |

---

|      |             |              |              |            |           |
|------|-------------|--------------|--------------|------------|-----------|
| C16  | 0.3442 (3)  | 0.1555 (2)   | 0.20782 (16) | 0.0488 (6) |           |
| C17  | 0.4439 (4)  | 0.0637 (2)   | 0.22588 (19) | 0.0623 (7) |           |
| H17  | 0.3849      | -0.0216      | 0.2213       | 0.075*     |           |
| C18  | 0.6297 (4)  | 0.0981 (3)   | 0.2506 (2)   | 0.0695 (8) |           |
| H18  | 0.6979      | 0.0362       | 0.2625       | 0.083*     |           |
| C19  | 0.7157 (4)  | 0.2251 (3)   | 0.2577 (2)   | 0.0665 (7) |           |
| H19  | 0.8423      | 0.2494       | 0.2755       | 0.080*     |           |
| C20  | 0.6147 (3)  | 0.3163 (2)   | 0.23847 (17) | 0.0532 (6) |           |
| H20  | 0.6748      | 0.4013       | 0.2430       | 0.064*     |           |
| C21  | 0.647 (3)   | 0.7469 (17)  | 0.4380 (15)  | 0.072 (6)  | 0.520 (8) |
| C22  | 0.753 (3)   | 0.8725 (19)  | 0.4286 (14)  | 0.124 (8)  | 0.520 (8) |
| H22A | 0.7762      | 0.8544       | 0.3663       | 0.186*     | 0.520 (8) |
| H22B | 0.8667      | 0.9015       | 0.4745       | 0.186*     | 0.520 (8) |
| H22C | 0.6831      | 0.9416       | 0.4389       | 0.186*     | 0.520 (8) |
| C23  | 0.565 (3)   | 0.805 (3)    | 0.5161 (11)  | 0.105 (7)  | 0.520 (8) |
| H23A | 0.6564      | 0.8702       | 0.5660       | 0.157*     | 0.520 (8) |
| H23B | 0.5143      | 0.7356       | 0.5393       | 0.157*     | 0.520 (8) |
| H23C | 0.4701      | 0.8471       | 0.4944       | 0.157*     | 0.520 (8) |
| C24  | 0.777 (3)   | 0.668 (2)    | 0.4817 (17)  | 0.171 (5)  | 0.520 (8) |
| H24A | 0.7085      | 0.6296       | 0.5198       | 0.205*     | 0.520 (8) |
| H24B | 0.7801      | 0.5927       | 0.4283       | 0.205*     | 0.520 (8) |
| C25  | 0.9450 (13) | 0.7029 (12)  | 0.5319 (9)   | 0.171 (5)  | 0.520 (8) |
| H25A | 1.0225      | 0.7434       | 0.4993       | 0.256*     | 0.520 (8) |
| H25B | 0.9861      | 0.6252       | 0.5413       | 0.256*     | 0.520 (8) |
| H25C | 0.9494      | 0.7659       | 0.5922       | 0.256*     | 0.520 (8) |
| C21A | 0.665 (4)   | 0.754 (2)    | 0.4492 (15)  | 0.076 (6)  | 0.480 (8) |
| C22A | 0.799 (2)   | 0.6604 (15)  | 0.4763 (10)  | 0.142 (8)  | 0.480 (8) |
| H22D | 0.8658      | 0.7005       | 0.5407       | 0.212*     | 0.480 (8) |
| H22E | 0.8830      | 0.6503       | 0.4353       | 0.212*     | 0.480 (8) |
| H22F | 0.7287      | 0.5741       | 0.4692       | 0.212*     | 0.480 (8) |
| C23A | 0.544 (4)   | 0.820 (3)    | 0.5231 (16)  | 0.136 (10) | 0.480 (8) |
| H23D | 0.4741      | 0.8750       | 0.4969       | 0.204*     | 0.480 (8) |
| H23E | 0.6245      | 0.8743       | 0.5820       | 0.204*     | 0.480 (8) |
| H23F | 0.4636      | 0.7503       | 0.5335       | 0.204*     | 0.480 (8) |
| C24A | 0.784 (3)   | 0.8687 (16)  | 0.4277 (14)  | 0.084 (5)  | 0.480 (8) |
| H24C | 0.7014      | 0.9185       | 0.4028       | 0.101*     | 0.480 (8) |
| H24D | 0.8568      | 0.9285       | 0.4879       | 0.101*     | 0.480 (8) |
| C25A | 0.8920 (15) | 0.8455 (10)  | 0.3726 (7)   | 0.128 (4)  | 0.480 (8) |
| H25D | 0.9835      | 0.8035       | 0.3980       | 0.192*     | 0.480 (8) |
| H25E | 0.9496      | 0.9282       | 0.3664       | 0.192*     | 0.480 (8) |
| H25F | 0.8247      | 0.7873       | 0.3116       | 0.192*     | 0.480 (8) |
| Cl2  | 0.10719 (9) | 0.10441 (6)  | 0.17580 (6)  | 0.0745 (2) |           |
| Cl1  | 0.15563 (9) | 0.72003 (8)  | -0.00583 (5) | 0.0713 (2) |           |
| N1   | 0.4263 (2)  | 0.47552 (17) | 0.15359 (13) | 0.0433 (4) |           |
| O1   | -0.0167 (2) | 0.55371 (18) | 0.24000 (15) | 0.0717 (5) |           |
| H1N  | 0.461 (3)   | 0.428 (2)    | 0.1038 (17)  | 0.054 (7)* |           |

---

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

|      | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$    |
|------|-------------|-------------|-------------|--------------|-------------|-------------|
| C1   | 0.0404 (11) | 0.0351 (10) | 0.0469 (12) | 0.0060 (9)   | 0.0096 (9)  | 0.0147 (9)  |
| C2   | 0.0461 (12) | 0.0391 (11) | 0.0580 (13) | 0.0172 (10)  | 0.0191 (10) | 0.0231 (10) |
| C3   | 0.0616 (14) | 0.0324 (10) | 0.0516 (13) | 0.0109 (10)  | 0.0202 (11) | 0.0157 (10) |
| C4   | 0.0573 (14) | 0.0387 (11) | 0.0478 (13) | 0.0085 (10)  | 0.0142 (11) | 0.0192 (10) |
| C5   | 0.0654 (15) | 0.0404 (11) | 0.0503 (13) | 0.0143 (11)  | 0.0229 (11) | 0.0224 (10) |
| C6   | 0.0508 (13) | 0.0365 (11) | 0.0656 (14) | 0.0079 (10)  | 0.0296 (11) | 0.0245 (10) |
| C7   | 0.0455 (12) | 0.0306 (10) | 0.0536 (13) | 0.0040 (9)   | 0.0142 (10) | 0.0151 (9)  |
| C8   | 0.0461 (14) | 0.0454 (12) | 0.0600 (14) | 0.0121 (10)  | 0.0226 (11) | 0.0168 (11) |
| C9   | 0.0432 (12) | 0.0318 (10) | 0.0406 (11) | 0.0083 (9)   | 0.0120 (9)  | 0.0119 (9)  |
| C10  | 0.0440 (13) | 0.0477 (12) | 0.0535 (13) | 0.0115 (10)  | 0.0130 (10) | 0.0226 (10) |
| C11  | 0.0452 (13) | 0.0586 (14) | 0.0659 (15) | 0.0032 (11)  | 0.0173 (12) | 0.0217 (13) |
| C12  | 0.0693 (17) | 0.0440 (12) | 0.0609 (15) | -0.0005 (12) | 0.0261 (13) | 0.0192 (11) |
| C13  | 0.0719 (17) | 0.0372 (11) | 0.0455 (12) | 0.0144 (11)  | 0.0191 (12) | 0.0176 (10) |
| C14  | 0.0481 (12) | 0.0381 (11) | 0.0405 (11) | 0.0124 (9)   | 0.0105 (9)  | 0.0117 (9)  |
| C15  | 0.0519 (13) | 0.0318 (10) | 0.0481 (12) | 0.0084 (9)   | 0.0195 (10) | 0.0141 (9)  |
| C16  | 0.0623 (14) | 0.0350 (11) | 0.0536 (13) | 0.0080 (10)  | 0.0231 (11) | 0.0160 (10) |
| C17  | 0.092 (2)   | 0.0373 (12) | 0.0723 (17) | 0.0202 (13)  | 0.0353 (15) | 0.0262 (12) |
| C18  | 0.090 (2)   | 0.0608 (16) | 0.0817 (19) | 0.0423 (16)  | 0.0340 (16) | 0.0373 (14) |
| C19  | 0.0578 (16) | 0.0714 (17) | 0.0844 (19) | 0.0266 (14)  | 0.0247 (14) | 0.0345 (15) |
| C20  | 0.0545 (15) | 0.0424 (12) | 0.0703 (16) | 0.0131 (11)  | 0.0219 (12) | 0.0231 (11) |
| C21  | 0.088 (9)   | 0.066 (9)   | 0.071 (9)   | 0.014 (8)    | -0.001 (6)  | 0.048 (8)   |
| C22  | 0.109 (12)  | 0.121 (12)  | 0.091 (10)  | -0.032 (8)   | -0.022 (8)  | 0.006 (8)   |
| C23  | 0.157 (13)  | 0.077 (7)   | 0.044 (7)   | 0.004 (9)    | -0.017 (9)  | -0.004 (6)  |
| C24  | 0.107 (6)   | 0.190 (8)   | 0.238 (11)  | 0.020 (6)    | -0.016 (6)  | 0.142 (8)   |
| C25  | 0.107 (6)   | 0.190 (8)   | 0.238 (11)  | 0.020 (6)    | -0.016 (6)  | 0.142 (8)   |
| C21A | 0.088 (10)  | 0.059 (8)   | 0.044 (6)   | -0.039 (7)   | -0.007 (6)  | 0.001 (5)   |
| C22A | 0.150 (12)  | 0.108 (7)   | 0.114 (7)   | -0.078 (8)   | -0.109 (8)  | 0.088 (6)   |
| C23A | 0.219 (19)  | 0.100 (14)  | 0.074 (9)   | -0.004 (12)  | 0.078 (11)  | -0.003 (8)  |
| C24A | 0.073 (7)   | 0.076 (8)   | 0.111 (11)  | -0.020 (5)   | 0.004 (6)   | 0.069 (8)   |
| C25A | 0.135 (9)   | 0.100 (6)   | 0.122 (8)   | 0.002 (6)    | 0.007 (7)   | 0.015 (6)   |
| Cl2  | 0.0669 (4)  | 0.0464 (3)  | 0.1071 (6)  | -0.0064 (3)  | 0.0240 (4)  | 0.0251 (3)  |
| Cl1  | 0.0531 (4)  | 0.0934 (5)  | 0.0785 (5)  | 0.0225 (4)   | 0.0065 (3)  | 0.0456 (4)  |
| N1   | 0.0528 (11) | 0.0326 (9)  | 0.0536 (11) | 0.0125 (8)   | 0.0256 (9)  | 0.0176 (8)  |
| O1   | 0.0477 (10) | 0.0753 (12) | 0.1089 (15) | 0.0197 (9)   | 0.0349 (10) | 0.0412 (11) |

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|       |           |         |           |
|-------|-----------|---------|-----------|
| C1—N1 | 1.461 (3) | C17—C18 | 1.364 (4) |
| C1—C9 | 1.516 (3) | C17—H17 | 0.9300    |
| C1—C2 | 1.554 (3) | C18—C19 | 1.378 (4) |
| C1—H1 | 0.9800    | C18—H18 | 0.9300    |
| C2—C8 | 1.505 (3) | C19—C20 | 1.380 (3) |
| C2—C3 | 1.536 (3) | C19—H19 | 0.9300    |
| C2—H2 | 0.9800    | C20—H20 | 0.9300    |
| C3—C4 | 1.534 (3) | C21—C23 | 1.46 (3)  |

|           |             |             |            |
|-----------|-------------|-------------|------------|
| C3—H3A    | 0.9700      | C21—C22     | 1.51 (3)   |
| C3—H3B    | 0.9700      | C21—C24     | 1.56 (3)   |
| C4—C21    | 1.454 (19)  | C22—H22A    | 0.9600     |
| C4—C5     | 1.535 (3)   | C22—H22B    | 0.9600     |
| C4—C21A   | 1.636 (19)  | C22—H22C    | 0.9600     |
| C4—H4     | 0.9800      | C23—H23A    | 0.9600     |
| C5—C6     | 1.539 (3)   | C23—H23B    | 0.9600     |
| C5—H5A    | 0.9700      | C23—H23C    | 0.9600     |
| C5—H5B    | 0.9700      | C24—C25     | 1.309 (18) |
| C6—C8     | 1.497 (3)   | C24—H24A    | 0.9700     |
| C6—C7     | 1.552 (3)   | C24—H24B    | 0.9700     |
| C6—H6     | 0.9800      | C25—H25A    | 0.9600     |
| C7—N1     | 1.467 (3)   | C25—H25B    | 0.9600     |
| C7—C15    | 1.511 (3)   | C25—H25C    | 0.9600     |
| C7—H7     | 0.9800      | C21A—C24A   | 1.55 (3)   |
| C8—O1     | 1.209 (3)   | C21A—C22A   | 1.61 (3)   |
| C9—C10    | 1.388 (3)   | C21A—C23A   | 1.64 (4)   |
| C9—C14    | 1.395 (3)   | C22A—H22D   | 0.9600     |
| C10—C11   | 1.381 (3)   | C22A—H22E   | 0.9600     |
| C10—H10   | 0.9300      | C22A—H22F   | 0.9600     |
| C11—C12   | 1.370 (4)   | C23A—H23D   | 0.9600     |
| C11—H11   | 0.9300      | C23A—H23E   | 0.9600     |
| C12—C13   | 1.371 (3)   | C23A—H23F   | 0.9600     |
| C12—H12   | 0.9300      | C24A—C25A   | 1.27 (3)   |
| C13—C14   | 1.384 (3)   | C24A—H24C   | 0.9700     |
| C13—H13   | 0.9300      | C24A—H24D   | 0.9700     |
| C14—C11   | 1.742 (2)   | C25A—H25D   | 0.9600     |
| C15—C20   | 1.384 (3)   | C25A—H25E   | 0.9600     |
| C15—C16   | 1.394 (3)   | C25A—H25F   | 0.9600     |
| C16—C17   | 1.374 (3)   | N1—H1N      | 0.89 (2)   |
| C16—C12   | 1.745 (2)   |             |            |
| N1—C1—C9  | 110.16 (16) | C16—C17—H17 | 120.1      |
| N1—C1—C2  | 109.81 (17) | C17—C18—C19 | 119.6 (2)  |
| C9—C1—C2  | 111.03 (16) | C17—C18—H18 | 120.2      |
| N1—C1—H1  | 108.6       | C19—C18—H18 | 120.2      |
| C9—C1—H1  | 108.6       | C18—C19—C20 | 120.3 (3)  |
| C2—C1—H1  | 108.6       | C18—C19—H19 | 119.9      |
| C8—C2—C3  | 108.14 (18) | C20—C19—H19 | 119.9      |
| C8—C2—C1  | 107.25 (16) | C19—C20—C15 | 121.5 (2)  |
| C3—C2—C1  | 115.74 (18) | C19—C20—H20 | 119.3      |
| C8—C2—H2  | 108.5       | C15—C20—H20 | 119.3      |
| C3—C2—H2  | 108.5       | C4—C21—C23  | 117.1 (18) |
| C1—C2—H2  | 108.5       | C4—C21—C22  | 113.0 (14) |
| C4—C3—C2  | 115.32 (17) | C23—C21—C22 | 100.3 (18) |
| C4—C3—H3A | 108.4       | C4—C21—C24  | 111.8 (14) |
| C2—C3—H3A | 108.4       | C23—C21—C24 | 102.4 (18) |
| C4—C3—H3B | 108.4       | C22—C21—C24 | 111 (2)    |



|             |             |                |            |
|-------------|-------------|----------------|------------|
| C2—C3—H3B   | 108.4       | C21—C22—H22A   | 109.4      |
| H3A—C3—H3B  | 107.5       | C21—C22—H22B   | 109.5      |
| C21—C4—C3   | 113.1 (6)   | H22A—C22—H22B  | 109.5      |
| C21—C4—C5   | 112.9 (9)   | C21—C22—H22C   | 109.5      |
| C3—C4—C5    | 110.78 (19) | H22A—C22—H22C  | 109.5      |
| C3—C4—C21A  | 114.5 (8)   | H22B—C22—H22C  | 109.5      |
| C5—C4—C21A  | 112.2 (9)   | C21—C23—H23A   | 109.5      |
| C21—C4—H4   | 106.5       | C21—C23—H23B   | 109.5      |
| C3—C4—H4    | 106.5       | H23A—C23—H23B  | 109.5      |
| C5—C4—H4    | 106.5       | C21—C23—H23C   | 109.4      |
| C4—C5—C6    | 115.05 (18) | H23A—C23—H23C  | 109.5      |
| C4—C5—H5A   | 108.5       | H23B—C23—H23C  | 109.5      |
| C6—C5—H5A   | 108.5       | C25—C24—C21    | 132.5 (17) |
| C4—C5—H5B   | 108.5       | C25—C24—H24A   | 103.9      |
| C6—C5—H5B   | 108.5       | C21—C24—H24A   | 103.9      |
| H5A—C5—H5B  | 107.5       | C25—C24—H24B   | 104.4      |
| C8—C6—C5    | 108.55 (17) | C21—C24—H24B   | 104.3      |
| C8—C6—C7    | 107.09 (18) | H24A—C24—H24B  | 105.5      |
| C5—C6—C7    | 115.73 (18) | C24—C25—H25A   | 109.3      |
| C8—C6—H6    | 108.4       | C24—C25—H25B   | 109.3      |
| C5—C6—H6    | 108.4       | H25A—C25—H25B  | 109.5      |
| C7—C6—H6    | 108.4       | C24—C25—H25C   | 109.8      |
| N1—C7—C15   | 109.85 (17) | H25A—C25—H25C  | 109.5      |
| N1—C7—C6    | 109.86 (16) | H25B—C25—H25C  | 109.5      |
| C15—C7—C6   | 112.34 (18) | C24A—C21A—C22A | 106 (2)    |
| N1—C7—H7    | 108.2       | C24A—C21A—C4   | 107.5 (15) |
| C15—C7—H7   | 108.2       | C22A—C21A—C4   | 105.6 (13) |
| C6—C7—H7    | 108.2       | C24A—C21A—C23A | 108.6 (19) |
| O1—C8—C6    | 124.7 (2)   | C22A—C21A—C23A | 120.0 (18) |
| O1—C8—C2    | 124.2 (2)   | C4—C21A—C23A   | 108.1 (18) |
| C6—C8—C2    | 111.14 (18) | C21A—C22A—H22D | 109.6      |
| C10—C9—C14  | 116.29 (18) | C21A—C22A—H22E | 109.3      |
| C10—C9—C1   | 121.34 (18) | H22D—C22A—H22E | 109.5      |
| C14—C9—C1   | 122.33 (18) | C21A—C22A—H22F | 109.5      |
| C11—C10—C9  | 121.6 (2)   | H22D—C22A—H22F | 109.5      |
| C11—C10—H10 | 119.2       | H22E—C22A—H22F | 109.5      |
| C9—C10—H10  | 119.2       | C21A—C23A—H23D | 109.5      |
| C12—C11—C10 | 120.7 (2)   | C21A—C23A—H23E | 109.5      |
| C12—C11—H11 | 119.7       | H23D—C23A—H23E | 109.5      |
| C10—C11—H11 | 119.7       | C21A—C23A—H23F | 109.4      |
| C11—C12—C13 | 119.5 (2)   | H23D—C23A—H23F | 109.5      |
| C11—C12—H12 | 120.2       | H23E—C23A—H23F | 109.5      |
| C13—C12—H12 | 120.2       | C25A—C24A—C21A | 121.8 (19) |
| C12—C13—C14 | 119.6 (2)   | C25A—C24A—H24C | 106.9      |
| C12—C13—H13 | 120.2       | C21A—C24A—H24C | 106.9      |
| C14—C13—H13 | 120.2       | C25A—C24A—H24D | 106.9      |
| C13—C14—C9  | 122.3 (2)   | C21A—C24A—H24D | 106.9      |
| C13—C14—Cl1 | 117.25 (17) | H24C—C24A—H24D | 106.7      |

|                 |              |                     |              |
|-----------------|--------------|---------------------|--------------|
| C9—C14—C11      | 120.43 (16)  | C24A—C25A—H25D      | 109.5        |
| C20—C15—C16     | 116.5 (2)    | C24A—C25A—H25E      | 109.5        |
| C20—C15—C7      | 121.22 (18)  | H25D—C25A—H25E      | 109.5        |
| C16—C15—C7      | 122.3 (2)    | C24A—C25A—H25F      | 109.5        |
| C17—C16—C15     | 122.3 (2)    | H25D—C25A—H25F      | 109.5        |
| C17—C16—C12     | 117.35 (18)  | H25E—C25A—H25F      | 109.5        |
| C15—C16—C12     | 120.29 (18)  | C1—N1—C7            | 114.20 (16)  |
| C18—C17—C16     | 119.8 (2)    | C1—N1—H1N           | 108.7 (16)   |
| C18—C17—H17     | 120.1        | C7—N1—H1N           | 108.5 (15)   |
|                 |              |                     |              |
| N1—C1—C2—C8     | -56.9 (2)    | C6—C7—C15—C20       | -95.7 (2)    |
| C9—C1—C2—C8     | -179.01 (17) | N1—C7—C15—C16       | -151.6 (2)   |
| N1—C1—C2—C3     | 63.8 (2)     | C6—C7—C15—C16       | 85.8 (2)     |
| C9—C1—C2—C3     | -58.2 (2)    | C20—C15—C16—C17     | -1.3 (3)     |
| C8—C2—C3—C4     | 53.9 (2)     | C7—C15—C16—C17      | 177.4 (2)    |
| C1—C2—C3—C4     | -66.4 (2)    | C20—C15—C16—C12     | -179.97 (17) |
| C2—C3—C4—C21    | -172.6 (12)  | C7—C15—C16—C12      | -1.3 (3)     |
| C2—C3—C4—C5     | -44.7 (2)    | C15—C16—C17—C18     | 0.8 (4)      |
| C2—C3—C4—C21A   | -172.9 (11)  | C12—C16—C17—C18     | 179.6 (2)    |
| C21—C4—C5—C6    | 172.3 (9)    | C16—C17—C18—C19     | 0.4 (4)      |
| C3—C4—C5—C6     | 44.4 (2)     | C17—C18—C19—C20     | -1.1 (4)     |
| C21A—C4—C5—C6   | 173.7 (10)   | C18—C19—C20—C15     | 0.6 (4)      |
| C4—C5—C6—C8     | -53.6 (2)    | C16—C15—C20—C19     | 0.6 (3)      |
| C4—C5—C6—C7     | 66.8 (2)     | C7—C15—C20—C19      | -178.1 (2)   |
| C8—C6—C7—N1     | 57.4 (2)     | C3—C4—C21—C23       | 70.0 (17)    |
| C5—C6—C7—N1     | -63.8 (2)    | C5—C4—C21—C23       | -56.8 (16)   |
| C8—C6—C7—C15    | -179.99 (17) | C21A—C4—C21—C23     | -120 (81)    |
| C5—C6—C7—C15    | 58.8 (2)     | C3—C4—C21—C22       | -46 (2)      |
| C5—C6—C8—O1     | -116.6 (3)   | C5—C4—C21—C22       | -172.5 (16)  |
| C7—C6—C8—O1     | 117.7 (2)    | C21A—C4—C21—C22     | 125 (82)     |
| C5—C6—C8—C2     | 63.0 (2)     | C3—C4—C21—C24       | -172.4 (14)  |
| C7—C6—C8—C2     | -62.6 (2)    | C5—C4—C21—C24       | 61 (2)       |
| C3—C2—C8—O1     | 116.6 (3)    | C21A—C4—C21—C24     | -2 (79)      |
| C1—C2—C8—O1     | -117.9 (2)   | C4—C21—C24—C25      | 148 (3)      |
| C3—C2—C8—C6     | -63.0 (2)    | C23—C21—C24—C25     | -86 (3)      |
| C1—C2—C8—C6     | 62.4 (2)     | C22—C21—C24—C25     | 20 (4)       |
| N1—C1—C9—C10    | -23.9 (3)    | C21—C4—C21A—C24A    | -63 (79)     |
| C2—C1—C9—C10    | 97.9 (2)     | C3—C4—C21A—C24A     | -53 (2)      |
| N1—C1—C9—C14    | 158.49 (18)  | C5—C4—C21A—C24A     | 179.7 (14)   |
| C2—C1—C9—C14    | -79.6 (2)    | C21—C4—C21A—C22A    | -176 (100)   |
| C14—C9—C10—C11  | 1.2 (3)      | C3—C4—C21A—C22A     | -166.3 (11)  |
| C1—C9—C10—C11   | -176.5 (2)   | C5—C4—C21A—C22A     | 66.3 (17)    |
| C9—C10—C11—C12  | -0.6 (4)     | C21—C4—C21A—C23A    | 54 (80)      |
| C10—C11—C12—C13 | -0.4 (4)     | C3—C4—C21A—C23A     | 64.1 (18)    |
| C11—C12—C13—C14 | 0.7 (3)      | C5—C4—C21A—C23A     | -63.3 (17)   |
| C12—C13—C14—C9  | -0.1 (3)     | C22A—C21A—C24A—C25A | 49 (2)       |
| C12—C13—C14—C11 | 179.93 (17)  | C4—C21A—C24A—C25A   | -64 (2)      |
| C10—C9—C14—C13  | -0.8 (3)     | C23A—C21A—C24A—C25A | 179.7 (17)   |

## supporting information

---

|                |             |              |             |
|----------------|-------------|--------------|-------------|
| C1—C9—C14—C13  | 176.83 (18) | C9—C1—N1—C7  | 179.34 (17) |
| C10—C9—C14—C11 | 179.14 (15) | C2—C1—N1—C7  | 56.8 (2)    |
| C1—C9—C14—C11  | -3.2 (3)    | C15—C7—N1—C1 | 178.90 (17) |
| N1—C7—C15—C20  | 27.0 (3)    | C6—C7—N1—C1  | -57.0 (2)   |

---