

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

***r*-1,*t*-3-Bis[4-(dimethylamino)phenyl]-*c*-2,*t*-4-bis(pyridin-4-yl)cyclobutane**

Shuguang Zhang and Junpeng Zhuang\*

Department of Organic Chemistry, Faculty of Science, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China  
Correspondence e-mail: zhuangjp@mail.buct.edu.cn

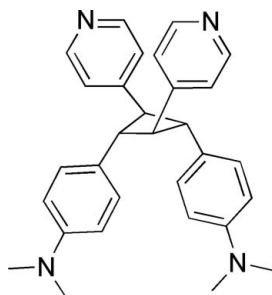
Received 9 May 2013; accepted 31 January 2014

Key indicators: single-crystal X-ray study;  $T = 113$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.045;  $wR$  factor = 0.121; data-to-parameter ratio = 18.7.

The title compound,  $\text{C}_{30}\text{H}_{32}\text{N}_4$ , was synthesized by the photodimerization of *trans*-4-[2-[4-(dimethylamino)phenyl]ethenyl]pyridine in benzene upon irradiation with UV light. This photodimer has a puckered cyclobutane ring with the four aryl substituents in an *r*-1,*t*-2,*c*-3,*t* conformation. The puckering angle of the cyclobutane ring is  $32.22$  ( $7$ )°, which is the largest among reported tetraaryl-substituted cyclobutanes. In the crystal, the molecules form a hollow, one-dimensional structure extending parallel to the *c* axis via two different pairs of  $\text{C}-\text{H}\cdots\pi$  interactions.

## Related literature

For the photodimerization of styrylpyridines, see: Horner & Hünig (1982); Quina & Whitten (1975); Zhang, Zhang, Zheng, Shen & Zhuang (2000). For the single-crystal structures of tetraaryl cyclobutanes and related molecules, see: Busetti *et al.* (1980); Coe *et al.* (2005); Li *et al.* (2007); Zhang *et al.* (1998); Zhang, Zhang, Zheng, Wang & Zhao (2000); Zhuang & Zheng (2002). For the synthesis of the monomer, see: Wang *et al.* (2005).



## Experimental

## Crystal data

$\text{C}_{30}\text{H}_{32}\text{N}_4$   
 $M_r = 448.60$

Monoclinic,  $C2/c$   
 $a = 23.166$  (5) Å

$b = 11.003$  (2) Å  
 $c = 9.6330$  (19) Å  
 $\beta = 91.67$  (3)°  
 $V = 2454.4$  (8) Å<sup>3</sup>  
 $Z = 4$

Mo  $K\alpha$  radiation  
 $\mu = 0.07$  mm<sup>-1</sup>  
 $T = 113$  K  
 $0.24 \times 0.20 \times 0.16$  mm

## Data collection

Rigaku Saturn 70 CCD diffractometer  
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2009)  
 $T_{\min} = 0.983$ ,  $T_{\max} = 0.989$

14966 measured reflections  
2934 independent reflections  
2335 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.043$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.121$   
 $S = 1.09$   
2934 reflections

157 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.26$  e Å<sup>-3</sup>

## Table 1

Hydrogen-bond geometry (Å, °).

$Cg1$  and  $Cg2$  are the centroids of the C8–C13 and N1/C1–C5 rings, respectively.

| $D-H\cdots A$                              | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{C15}-\text{H15B}\cdots\text{Cg1}^i$ | 0.96  | 2.82        | 3.679 (2)   | 149           |
| $\text{C12}-\text{H12}\cdots\text{Cg2}^i$  | 0.96  | 3.12        | 4.104 (2)   | 161           |

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

Data collection: *CrystalClear* (Rigaku, 2009); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was supported by the Youth Foundation of Beijing University of Chemical Technology.

Supporting information for this paper is available from the IUCr electronic archives (Reference: MW2110).

## References

- Busetti, V., Valle, G., Zanotti, G. & Galiazzo, G. (1980). *Acta Cryst.* **B36**, 894–897.  
Coe, B. J., Hall, J. J., Harris, J. A., Brunshwig, B. S., Coles, S. J. & Hursthouse, M. B. (2005). *Acta Cryst.* **E61**, o464–o467.  
Horner, M. & Hünig, S. (1982). *Liebigs Ann. Chem.* **6**, 1183–1192.  
Li, F.-Y., Wang, S.-T., Zhuang, J.-P., Jiang, L. & Song, Y.-L. (2007). *Acta Cryst.* **E63**, o1171–o1172.  
Quina, F. H. & Whitten, D. G. (1975). *J. Am. Chem. Soc.* **97**, 1602–1603.  
Rigaku (2009). *CrystalClear*. Rigaku Americas Corporation, The Woodlands, Texas, USA.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
Wang, S. L., Gao, G. Y., Ho, T. I. & Yang, L. Y. (2005). *Chem. Phys. Lett.* **415**, 217–222.  
Zhang, W. Q., Zhang, M. J., Wang, J. X., Yang, X. R., Wang, S. L., Jiang, Q. & An, Y. (1998). *Acta Chim. Sin.* **56**, 612–617.  
Zhang, W. Q., Zhang, X. H., Zheng, Y., Shen, G. & Zhuang, J. P. (2000). *Photograph. Sci. Photochem.* **18**, 144–147.  
Zhang, W. Q., Zhang, Z. M., Zheng, Y., Wang, S. L. & Zhao, S. N. (2000). *Acta Phys. Chim. Sin.* **16**, 207–213.  
Zhuang, J.-P. & Zheng, Y. (2002). *Acta Cryst.* **E58**, o1195–o1197.

## supporting information

*Acta Cryst.* (2014). E70, o311 [doi:10.1107/S1600536814002311]

***r*-1,*t*-3-Bis[4-(dimethylamino)phenyl]-*c*-2,*t*-4-bis(pyridin-4-yl)cyclobutane****Shuguang Zhang and Junpeng Zhuang****S1. Comment**

The photodimerization of styrylpyridines has been studied extensively in the past few decades (Horner & Hünig, 1982; Quina & Whitten, 1975; Zhang, Zhang, Zheng, Shen & Zhuang, 2000). As the protonation of the pyridine ring increases the solubility and dipolar interactions of styrylpyridines in water, most photodimerization reactions were carried out in acidic aqueous solution. The main tetraaryl substituted cyclobutane photodimers usually have head-to-tail central symmetric structures. However, the photodimerization of *trans*-4-[2-(4-dimethylaminophenyl)ethenyl]pyridine (**A**) in acidic aqueous solution failed (Zhang, Zhang, Zheng, Shen & Zhuang, 2000). Herein, the photodimerization of **A** was carried out in benzene and the photodimer (**2A**, Fig. 1) was successfully synthesized in 37% yield.

The structure of **2A** shows that the four aryl substituents adopt the *r*-1,*t*-2,*c*-3,*t*-4 conformation, whereas the styrylpyridine photodimers synthesized in acidic aqueous solution adopt the head-to-tail *r*-1,*c*-2,*t*-3,*t*-4 conformation. In addition, the photodimer of 2-[2-(4-dimethylaminophenyl)ethenyl]benzoxazole synthesized in acetonitrile also adopts the head-to-tail *r*-1,*c*-2,*t*-3,*t*-4 conformation (Li *et al.*, 2007). This difference is ascribed to solvent effects. The steric hindrance of the dimethylamino groups prevents **A** to align in a parallel manner in the non-polar benzene solvent, resulting in the all *trans* conformation of the adjacent aryl groups in **2A**.

Several styrylpyridine photodimers such as *r*-1,*c*-2,*t*-3,*t*-4-1,3-bis[2-(4-*R*-phenyl)]-2,4-di(pyridin-4-yl)cyclobutane (*R*=Cl, CH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>) have been reported (Busetti *et al.*, 1980; Zhang *et al.*, 1998; Zhang, Zhang, Zheng, Wang & Zhao, 2000). The average dihedral angles of the cyclobutane rings are 19.2, 24.6 and 16.4°, respectively. In addition, the *trans*-head-to-head photodimer of 1-(4-methoxyphenyl)-2-(5-phenyl-1,3,4-oxadiazolyl)ethene also has a puckered cyclobutane ring with a dihedral angle of 30° (Zhuang & Zheng, 2002). Though the adjacent aryl groups of **2A** adopt the all *trans* conformation, the dihedral angle of the cyclobutane ring is 32.22 (7)° which is the largest one among reported tetraaryl substituted cyclobutanes.

The C6—C7 and C6—C7A bond distances are 1.5594 (16) Å and 1.5519 (16) Å, and the C3—C6 and C7—C8 bond distances are 1.4962 (18) Å and 1.5011 (16) Å, which are similar to the corresponding bond distances in other tetraaryl substituted cyclobutanes (Zhang *et al.*, 1998; Zhang, Zhang, Zheng, Wang & Zhao, 2000). The two phenyl rings (C8—C9—C10—C11—C12—C13 and C8A—C9A—C10A—C11A—C12A—C13A) are almost coplanar with the dihedral angle between them being only 1.78 (7)°.

The dimethylamino plane and the phenyl ring (C8—C9—C10—C11—C12—C13) are not coplanar, the torsion angle (C14—N2—C11—C10) is 17.48 (18)° which is larger than that in *c*-2, *t*-4-bis(2-benzoxazol-2-yl)-*r*-1,*t*-3-bis[4-(dimethylamino)phenyl]cyclobutane (Li *et al.*, 2007). The distances of the two methyl groups (C14 and C15) from the mean plane of the phenyl ring are 0.2629 (22) and 0.2335 (22) Å respectively, indicating that the lone electron pair of the N atom is not completely conjugated with the phenyl ring. While the dimethylaminophenyl ring in *trans*-4-[(4-dimethylaminophenyl)ethenyl]-*N*-methylquinolinium *p*-toluenesulfonate monohydrate (Coe *et al.*, 2005) is essentially planar because of the strong *p*- $\pi$  conjugation between the dimethylamino group and the planar diarylethene molecule.

As shown in Figure 2, the molecules of **2A** pack with each other to form a hollow, one-dimensional structure along the *c* axis. This arrangement appears to be directed by two sets of C—H $\cdots$  $\pi$  interactions with that involving H15B stronger than that using H12 (Table 1).

## S2. Experimental

**A** was synthesized according to the literature (Wang *et al.*, 2005) and 1.97 g (8.78 mmol) was dissolved in 200 mL of benzene and irradiated with a water-cooled 125 W medium-pressure mercury lamp which was immersed in the solution. After irradiation for about 30 h, the solvent was evaporated to dryness and the crude product was separated by column chromatography (ethyl acetate: dichloromethane = 1: 1) to give 0.73 g of colorless crystals of **2A**. Yield, 37%; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.35 (d, 4H, *J*=4.8 Hz), 7.00 (d, 4H, *J*=4.8 Hz), 6.94 (d, 4H, *J*=6.4 Hz), 6.53 (d, 4H, *J*=6.4 Hz), 4.38 (d, 2H, *J*=9.0 Hz), 74.28 (d, 2H, *J*=9.0 Hz) p.p.m.. The single-crystal of **2A**, suitable for X-ray analysis, was grown by slow evaporation of a methanol solution of **2A**.

## S3. Refinement

H atoms were placed in calculated positions [C—H = 0.93–0.97 Å] and allowed to ride on the parent atoms, with  $U_{\text{iso}}$  values constrained to be 1.2 $U_{\text{eq}}$  of the parent atom.

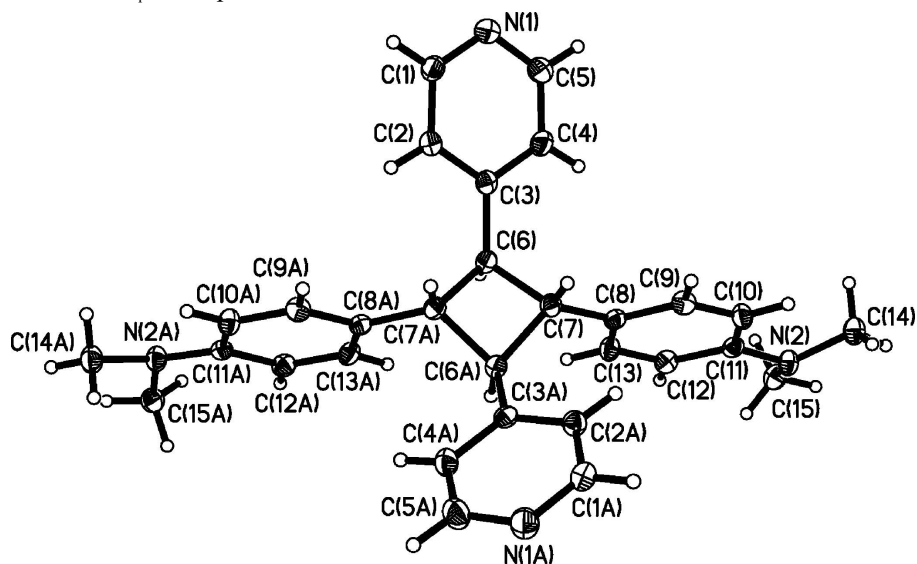


Figure 1

Molecular structure of **2A**. Displacement ellipsoids are drawn at the 50% probability level.

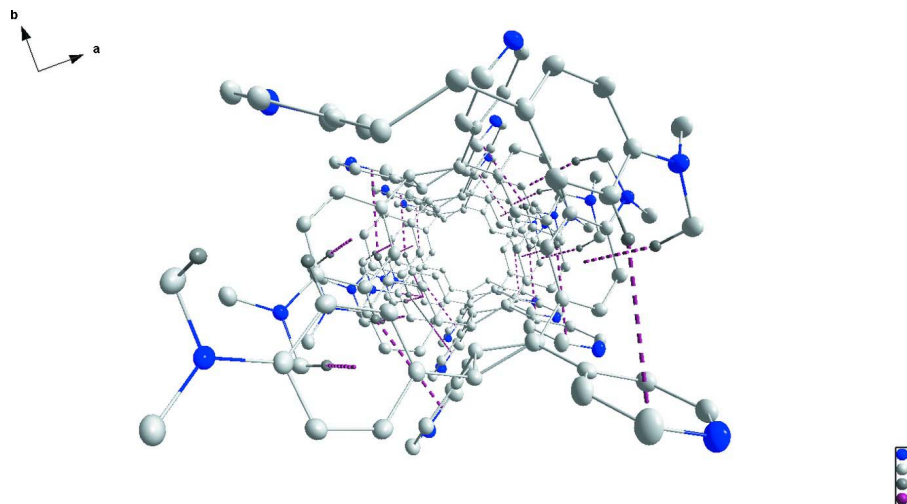


Figure 2

Packing diagram of **2A** viewed along *c* axis.

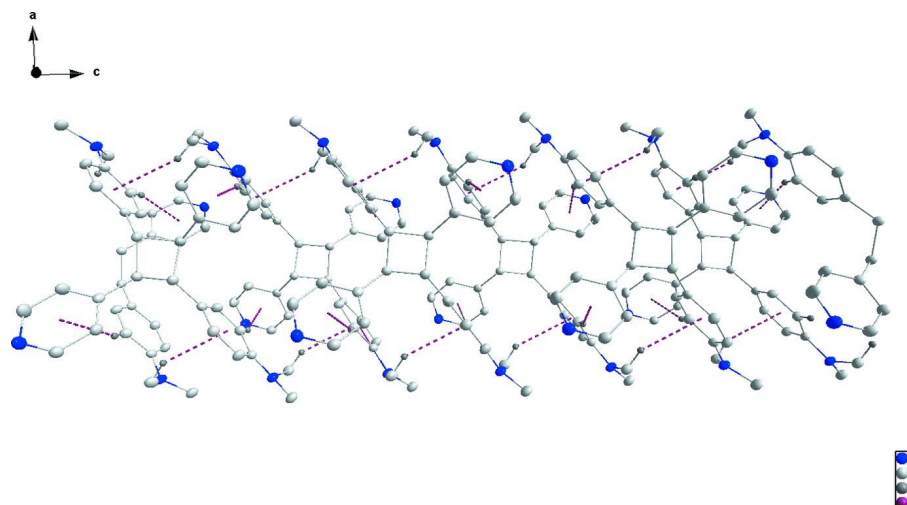


Figure 3

Packing diagram of **2A** viewed along *b* axis.

***r*-1,*t*-3-Bis[4-(dimethylamino)phenyl]-*c*-2,*t*-4-bis(pyridin-4-yl)cyclobutane**

*Crystal data*

$C_{30}H_{32}N_4$

$M_r = 448.60$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 23.166\ (5)\ \text{\AA}$

$b = 11.003\ (2)\ \text{\AA}$

$c = 9.6330\ (19)\ \text{\AA}$

$\beta = 91.67\ (3)^\circ$

$V = 2454.4\ (8)\ \text{\AA}^3$

$Z = 4$

$F(000) = 960$

$D_x = 1.214\ \text{Mg m}^{-3}$

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

Cell parameters from 2660 reflections

$\theta = 1.8\text{--}27.9^\circ$

$\mu = 0.07\ \text{mm}^{-1}$

$T = 113\ \text{K}$

Block, colourless

$0.24 \times 0.20 \times 0.16\ \text{mm}$

*Data collection*

|   |  |
|---|--|
| Rigaku Saturn 70 CCD diffractometer                                     | 14966 measured reflections   |
| Radiation source: rotating anode  | 2934 independent reflections   |
| Confocal monochromator  | 2335 reflections with $I > 2\sigma(I)$                                 |
| $\omega$ scans  | $R_{\text{int}} = 0.043$   |
| Absorption correction: multi-scan ( <i>CrystalClear</i> ; Rigaku, 2009) | $\theta_{\text{max}} = 27.9^\circ$ , $\theta_{\text{min}} = 1.8^\circ$ |
| $T_{\text{min}} = 0.983$ , $T_{\text{max}} = 0.989$                     | $h = -30 \rightarrow 30$   |
|   | $k = -14 \rightarrow 14$   |
|   | $l = -12 \rightarrow 12$   |

*Refinement*

|  |   |
|--|---|
| Refinement on $F^2$  | Hydrogen site location: inferred from neighbouring sites  |
| Least-squares matrix: full                                     | H-atom parameters constrained   |
| $R[F^2 > 2\sigma(F^2)] = 0.045$                                | $w = 1/[\sigma^2(F_o^2) + (0.0689P)^2]$   |
| $wR(F^2) = 0.121$  | where $P = (F_o^2 + 2F_c^2)/3$  |
| $S = 1.09$   | $(\Delta/\sigma)_{\text{max}} < 0.001$  |
| 2934 reflections   | $\Delta\rho_{\text{max}} = 0.24 \text{ e } \text{\AA}^{-3}$   |
| 157 parameters   | $\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{\AA}^{-3}$  |
| 0 restraints   | Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.0115 (17)   |
| Secondary atom site location: difference Fourier map           |   |

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 ( $\text{\AA}^2$ )*

|    | $x$          | $y$          | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|--------------|--------------|----------------------------------|
| N1 | -0.12781 (4) | 0.08386 (9)  | 0.34546 (11) | 0.0261 (3)                       |
| N2 | 0.21597 (4)  | 0.48468 (8)  | 0.38134 (10) | 0.0201 (3)                       |
| C1 | -0.14278 (5) | 0.08343 (11) | 0.47858 (13) | 0.0215 (3)                       |
| H1 | -0.1758      | 0.0408       | 0.5017       | 0.026*                           |
| C2 | -0.11207 (5) | 0.14263 (10) | 0.58397 (12) | 0.0191 (3)                       |
| H2 | -0.1241      | 0.1375       | 0.6750       | 0.023*                           |
| C3 | -0.06316 (5) | 0.20975 (10) | 0.55322 (12) | 0.0166 (3)                       |
| C4 | -0.04739 (5) | 0.21074 (11) | 0.41486 (12) | 0.0233 (3)                       |
| H4 | -0.0151      | 0.2541       | 0.3884       | 0.028*                           |
| C5 | -0.08012 (6) | 0.14681 (12) | 0.31670 (13) | 0.0289 (3)                       |
| H5 | -0.0683      | 0.1477       | 0.2253       | 0.035*                           |
| C6 | -0.02904 (5) | 0.27871 (10) | 0.66140 (12) | 0.0170 (3)                       |
| H6 | -0.0342      | 0.3661       | 0.6456       | 0.020*                           |
| C7 | 0.03660 (4)  | 0.25051 (10) | 0.68241 (11) | 0.0165 (3)                       |
| H7 | 0.0421       | 0.1627       | 0.6722       | 0.020*                           |

|      |             |              |              |            |
|------|-------------|--------------|--------------|------------|
| C8   | 0.08169 (5) | 0.31420 (10) | 0.60052 (11) | 0.0165 (3) |
| C9   | 0.12213 (5) | 0.24764 (10) | 0.52824 (12) | 0.0191 (3) |
| H9   | 0.1200      | 0.1633       | 0.5298       | 0.023*     |
| C10  | 0.16550 (5) | 0.30229 (10) | 0.45398 (12) | 0.0204 (3) |
| H10  | 0.1914      | 0.2541       | 0.4065       | 0.024*     |
| C11  | 0.17092 (5) | 0.42906 (10) | 0.44948 (11) | 0.0172 (3) |
| C12  | 0.12953 (5) | 0.49722 (10) | 0.52068 (12) | 0.0196 (3) |
| H12  | 0.1312      | 0.5816       | 0.5186       | 0.023*     |
| C13  | 0.08643 (5) | 0.44051 (11) | 0.59377 (12) | 0.0193 (3) |
| H13  | 0.0599      | 0.4881       | 0.6397       | 0.023*     |
| C14  | 0.24760 (5) | 0.41298 (11) | 0.28156 (13) | 0.0240 (3) |
| H14A | 0.2213      | 0.3836       | 0.2103       | 0.036*     |
| H14B | 0.2658      | 0.3453       | 0.3281       | 0.036*     |
| H14C | 0.2766      | 0.4628       | 0.2405       | 0.036*     |
| C15  | 0.21211 (5) | 0.61429 (10) | 0.35107 (13) | 0.0230 (3) |
| H15A | 0.2091      | 0.6588       | 0.4363       | 0.034*     |
| H15B | 0.1786      | 0.6297       | 0.2927       | 0.034*     |
| H15C | 0.2461      | 0.6398       | 0.3043       | 0.034*     |

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

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|-----|------------|------------|------------|-------------|-------------|-------------|
| N1  | 0.0243 (6) | 0.0315 (6) | 0.0226 (6) | -0.0049 (5) | 0.0012 (4)  | -0.0045 (5) |
| N2  | 0.0177 (5) | 0.0189 (5) | 0.0240 (5) | -0.0004 (4) | 0.0060 (4)  | 0.0021 (4)  |
| C1  | 0.0181 (6) | 0.0226 (6) | 0.0239 (6) | -0.0010 (5) | 0.0020 (5)  | -0.0015 (5) |
| C2  | 0.0185 (6) | 0.0205 (6) | 0.0185 (6) | 0.0006 (4)  | 0.0026 (5)  | -0.0006 (5) |
| C3  | 0.0156 (5) | 0.0155 (5) | 0.0186 (6) | 0.0037 (4)  | 0.0004 (4)  | 0.0003 (4)  |
| C4  | 0.0193 (6) | 0.0292 (7) | 0.0215 (6) | -0.0045 (5) | 0.0033 (5)  | 0.0011 (5)  |
| C5  | 0.0278 (7) | 0.0404 (8) | 0.0185 (6) | -0.0058 (6) | 0.0036 (5)  | -0.0033 (6) |
| C6  | 0.0144 (5) | 0.0190 (6) | 0.0176 (6) | -0.0004 (4) | 0.0009 (4)  | 0.0006 (5)  |
| C7  | 0.0155 (6) | 0.0158 (6) | 0.0181 (6) | 0.0014 (4)  | 0.0015 (5)  | -0.0004 (4) |
| C8  | 0.0137 (5) | 0.0204 (6) | 0.0154 (6) | -0.0003 (4) | -0.0006 (4) | 0.0003 (5)  |
| C9  | 0.0201 (6) | 0.0158 (6) | 0.0215 (6) | -0.0002 (4) | 0.0023 (5)  | 0.0004 (5)  |
| C10 | 0.0193 (6) | 0.0198 (6) | 0.0224 (6) | 0.0019 (5)  | 0.0057 (5)  | -0.0020 (5) |
| C11 | 0.0146 (5) | 0.0199 (6) | 0.0173 (6) | -0.0006 (4) | 0.0000 (4)  | 0.0019 (5)  |
| C12 | 0.0193 (6) | 0.0159 (6) | 0.0234 (6) | 0.0009 (4)  | 0.0005 (5)  | 0.0012 (5)  |
| C13 | 0.0157 (5) | 0.0187 (6) | 0.0237 (6) | 0.0027 (4)  | 0.0031 (5)  | -0.0002 (5) |
| C14 | 0.0210 (6) | 0.0267 (7) | 0.0247 (7) | -0.0009 (5) | 0.0076 (5)  | 0.0015 (5)  |
| C15 | 0.0213 (6) | 0.0214 (6) | 0.0264 (7) | -0.0023 (5) | 0.0034 (5)  | 0.0047 (5)  |

*Geometric parameters (Å, °)*

|        |             |                    |             |
|--------|-------------|--------------------|-------------|
| N1—C1  | 1.3381 (15) | C7—C6 <sup>i</sup> | 1.5512 (15) |
| N1—C5  | 1.3396 (16) | C7—H7              | 0.9800      |
| N2—C11 | 1.3908 (14) | C8—C9              | 1.3918 (15) |
| N2—C14 | 1.4576 (15) | C8—C13             | 1.3958 (16) |
| N2—C15 | 1.4579 (14) | C9—C10             | 1.3874 (15) |
| C1—C2  | 1.3853 (17) | C9—H9              | 0.9300      |

|                        |             |                            |              |
|------------------------|-------------|----------------------------|--------------|
| C1—H1                  | 0.9300      | C10—C11                    | 1.4013 (16)  |
| C2—C3                  | 1.3916 (15) | C10—H10                    | 0.9300       |
| C2—H2                  | 0.9300      | C11—C12                    | 1.4109 (16)  |
| C3—C4                  | 1.3923 (16) | C12—C13                    | 1.3867 (16)  |
| C3—C6                  | 1.4961 (16) | C12—H12                    | 0.9300       |
| C4—C5                  | 1.3863 (17) | C13—H13                    | 0.9300       |
| C4—H4                  | 0.9300      | C14—H14A                   | 0.9600       |
| C5—H5                  | 0.9300      | C14—H14B                   | 0.9600       |
| C6—C7 <sup>i</sup>     | 1.5512 (15) | C14—H14C                   | 0.9600       |
| C6—C7                  | 1.5593 (15) | C15—H15A                   | 0.9600       |
| C6—H6                  | 0.9800      | C15—H15B                   | 0.9600       |
| C7—C8                  | 1.5008 (15) | C15—H15C                   | 0.9600       |
|                        |             |                            |              |
| C1—N1—C5               | 116.00 (11) | C9—C8—C13                  | 116.46 (10)  |
| C11—N2—C14             | 118.14 (10) | C9—C8—C7                   | 120.41 (10)  |
| C11—N2—C15             | 118.84 (9)  | C13—C8—C7                  | 123.12 (10)  |
| C14—N2—C15             | 115.26 (9)  | C10—C9—C8                  | 122.55 (11)  |
| N1—C1—C2               | 123.96 (11) | C10—C9—H9                  | 118.7        |
| N1—C1—H1               | 118.0       | C8—C9—H9                   | 118.7        |
| C2—C1—H1               | 118.0       | C9—C10—C11                 | 120.95 (10)  |
| C1—C2—C3               | 119.84 (11) | C9—C10—H10                 | 119.5        |
| C1—C2—H2               | 120.1       | C11—C10—H10                | 119.5        |
| C3—C2—H2               | 120.1       | N2—C11—C10                 | 121.45 (10)  |
| C2—C3—C4               | 116.48 (11) | N2—C11—C12                 | 121.70 (10)  |
| C2—C3—C6               | 122.53 (10) | C10—C11—C12                | 116.83 (10)  |
| C4—C3—C6               | 120.99 (10) | C13—C12—C11                | 121.14 (11)  |
| C5—C4—C3               | 119.70 (11) | C13—C12—H12                | 119.4        |
| C5—C4—H4               | 120.2       | C11—C12—H12                | 119.4        |
| C3—C4—H4               | 120.2       | C12—C13—C8                 | 122.04 (10)  |
| N1—C5—C4               | 124.00 (11) | C12—C13—H13                | 119.0        |
| N1—C5—H5               | 118.0       | C8—C13—H13                 | 119.0        |
| C4—C5—H5               | 118.0       | N2—C14—H14A                | 109.5        |
| C3—C6—C7 <sup>i</sup>  | 120.12 (9)  | N2—C14—H14B                | 109.5        |
| C3—C6—C7               | 118.86 (9)  | H14A—C14—H14B              | 109.5        |
| C7 <sup>i</sup> —C6—C7 | 88.36 (9)   | N2—C14—H14C                | 109.5        |
| C3—C6—H6               | 109.3       | H14A—C14—H14C              | 109.5        |
| C7 <sup>i</sup> —C6—H6 | 109.3       | H14B—C14—H14C              | 109.5        |
| C7—C6—H6               | 109.3       | N2—C15—H15A                | 109.5        |
| C8—C7—C6 <sup>i</sup>  | 121.09 (10) | N2—C15—H15B                | 109.5        |
| C8—C7—C6               | 121.99 (9)  | H15A—C15—H15B              | 109.5        |
| C6 <sup>i</sup> —C7—C6 | 87.07 (9)   | N2—C15—H15C                | 109.5        |
| C8—C7—H7               | 108.2       | H15A—C15—H15C              | 109.5        |
| C6 <sup>i</sup> —C7—H7 | 108.2       | H15B—C15—H15C              | 109.5        |
| C6—C7—H7               | 108.2       |                            |              |
|                        |             |                            |              |
| C5—N1—C1—C2            | -0.30 (18)  | C6—C7—C8—C9                | -126.96 (12) |
| N1—C1—C2—C3            | 1.49 (18)   | C6 <sup>i</sup> —C7—C8—C13 | -53.68 (15)  |
| C1—C2—C3—C4            | -1.27 (16)  | C6—C7—C8—C13               | 54.16 (16)   |

|  |              |                 |              |
|--|--------------|-----------------|--------------|
| C1—C2—C3—C6                            | 178.20 (11)  | C13—C8—C9—C10   | 0.62 (18)    |
| C2—C3—C4—C5                            | 0.03 (17)    | C7—C8—C9—C10    | -178.34 (10) |
| C6—C3—C4—C5                            | -179.44 (11) | C8—C9—C10—C11   | 0.61 (19)    |
| C1—N1—C5—C4                            | -1.05 (19)   | C14—N2—C11—C10  | 17.54 (17)   |
| C3—C4—C5—N1                            | 1.2 (2)      | C15—N2—C11—C10  | 165.43 (11)  |
| C2—C3—C6—C7 <sup>i</sup>               | 16.79 (16)   | C14—N2—C11—C12  | -164.33 (11) |
| C4—C3—C6—C7 <sup>i</sup>               | -163.77 (10) | C15—N2—C11—C12  | -16.44 (17)  |
| C2—C3—C6—C7                            | 123.18 (12)  | C9—C10—C11—N2   | 176.66 (11)  |
| C4—C3—C6—C7                            | -57.38 (15)  | C9—C10—C11—C12  | -1.55 (17)   |
| C3—C6—C7—C8                            | 88.20 (13)   | N2—C11—C12—C13  | -176.89 (11) |
| C7 <sup>i</sup> —C6—C7—C8              | -147.91 (9)  | C10—C11—C12—C13 | 1.32 (17)    |
| C3—C6—C7—C6 <sup>i</sup>               | -146.52 (8)  | C11—C12—C13—C8  | -0.12 (18)   |
| C7 <sup>i</sup> —C6—C7—C6 <sup>i</sup> | -22.63 (11)  | C9—C8—C13—C12   | -0.86 (17)   |
| C6 <sup>i</sup> —C7—C8—C9              | 125.21 (12)  | C7—C8—C13—C12   | 178.07 (11)  |

Symmetry code: (i)  $-x, y, -z+3/2$ .

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

Cg1 and Cg2 are the centroids of the C8—C13 and N1/C1—C5 rings, respectively.

| $D-H\cdots A$                       | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|-------|-------------|-------------|---------------|
| C15—H15B $\cdots$ Cg1 <sup>ii</sup> | 0.96  | 2.82        | 3.679 (2)   | 149           |
| C12—H12 $\cdots$ Cg2 <sup>ii</sup>  | 0.96  | 3.12        | 4.104 (2)   | 161           |

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