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# Crystal structure of 4-bromo-*N*-[(3,6-di-*tert*-butyl-9*H*-carbazol-1-yl)methylidene]aniline

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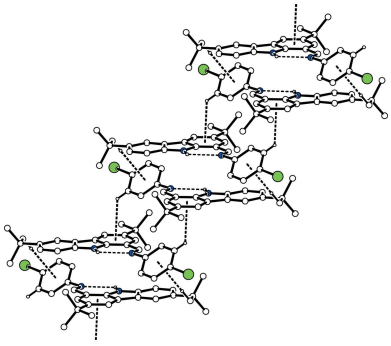
In the title compound, $C_{27}H_{29}BrN_2$, the carbazole ring system is essentially planar, with an r.m.s. deviation of 0.0781 (16) Å. An intramolecular N—H···N hydrogen bond forms an *S*(6) ring motif. One of the *tert*-butyl substituents shows rotational disorder over two sites with occupancies of 0.592 (3) and 0.408 (3). In the crystal, two molecules are associated into an inversion dimer through a pair of C—H···$\pi$ interactions. The dimers are further linked by another pair of C—H···$\pi$ interactions, forming a ribbon along the *c*-axis direction. A C—H···$\pi$ interaction involving the minor disordered component and the carbazole ring system links the ribbons, generating a network sheet parallel to (100).

## 1. Chemical context

Carbazole derivatives have been widely applied in various fields such as pharmaceuticals (Obora, 2018), electroluminescent materials (Krucaite & Grigalevicius, 2019; Taneda, *et al.*, 2015) and dyes (Zhao *et al.*, 2019). As a result of the high acidity of the N—H bond, 9*H*-carbazoles have also attracted much attention as hydrogen donors in hydrogen-bonding systems (Rubio *et al.*, 2015; Wiosna-Sałyga *et al.*, 2006). Substitution of the 1 position of 9*H*-carbazole with a hydrogen acceptor can afford an intramolecular hydrogen-bonding system in the molecules. In this work, a Schiff base including carbazole, *N*-(3,6-di-*tert*-butyl-9*H*-calbazol-1-yl-methylidene)-4-bromoaniline, is newly synthesized. 3,6-Di-*tert*-butyl-9*H*-carbazole is useful in order to substitute the 1-position of the 9*H*-carbazole moiety because the substitution reaction would only occur at its 1- and 8-positions. Thus, the title compound has two *tert*-butyl groups on the carbazole moiety. The title compound is a suitable model to investigate an intramolecular hydrogen bond between the heteroaromatic N—H and the N atom of the imino group. We report herein on its molecular and crystal structures.



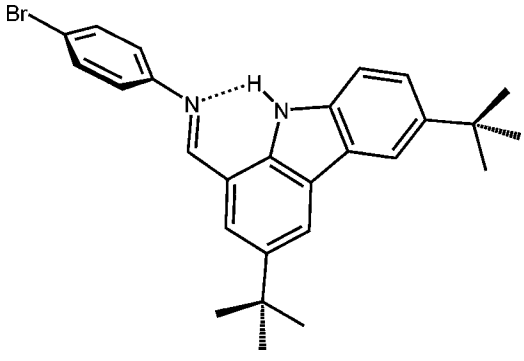


**Table 1**
Hydrogen-bond geometry (Å, °).

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the C25–C30, C4–C9 and N3/C4/C5/C11/C10 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···N2 | 0.76 (2) | 2.39 (2) | 2.862 (2) | 121.3 (16) |
| C22*A*—H22*C*···*Cg*1$^{i}$ | 0.96 | 2.92 | 3.878 (4) | 177 |
| C29—H29···*Cg*2$^{ii}$ | 0.93 | 2.95 | 3.613 (2) | 129 |
| C21*B*—H21*E*···*Cg*1$^{i}$ | 0.96 | 2.62 | 3.391 (5) | 138 |
| C22*B*—H22*D*···*Cg*3$^{iii}$ | 0.96 | 2.92 | 3.839 (5) | 159 |

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

## 2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The molecule adopts an *E* configuration with respect to the C=N double bond. The carbazole ring is almost planar with a maximum deviation of 0.0781 (16) Å at atom C8. There is an intramolecular N—H···N hydrogen bond involving the amino group (N3—H3) in the carbazole ring and an imine N atom (N2), generating an *S*(6) ring motif (Table 1). The dihedral angle between the mean planes of the carbazole ring system and the benzene C25–C30 ring is 42.72 (7)°. The bond lengths and angles of the title compound are normal and agree with those values in other carbazole imine compounds (Gibson *et al.*, 2003; Nolla-Saltiel *et al.*, 2018). One of the *tert*-butyl substituents shows rotational disorder around the C13—C20 bond axis over two sites with occupancies of 0.592 (3) and 0.408 (3).

## 3. Supramolecular features

In the crystal, two molecules are associated through a pair of C—H···$\pi$ interactions (C22*A*—H22*C*···*Cg*1$^{i}$ in the major disorder component or C21*B*—H21*E*···*Cg*1$^{i}$ in the minor disorder component; *Cg*1 is the centroid of the C25–C30 ring; symmetry code as in Table 1), forming a centrosymmetric dimer. The dimers are linked by another pair of C—H···$\pi$ interactions (C29—H29···*Cg*2$^{ii}$; *Cg*2 is the centroid of the C4–C9 ring; symmetry code as in Table 1), forming a ribbon along the *c*-axis direction (Fig. 2). These ribbons are linked *via* a C—H···$\pi$ interaction involving the minor disorder component

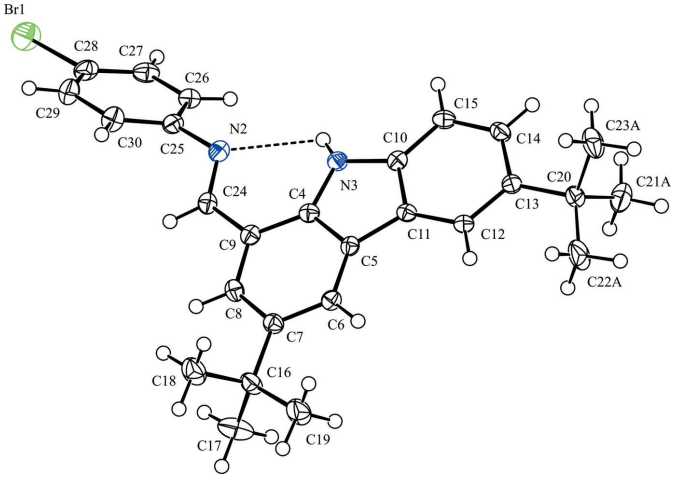



**Figure 1**
The molecular structure of the title compound, with atom labelling. Only the major disordered component is shown. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radius. The intramolecular N—H···N hydrogen bond is shown as a dashed line.

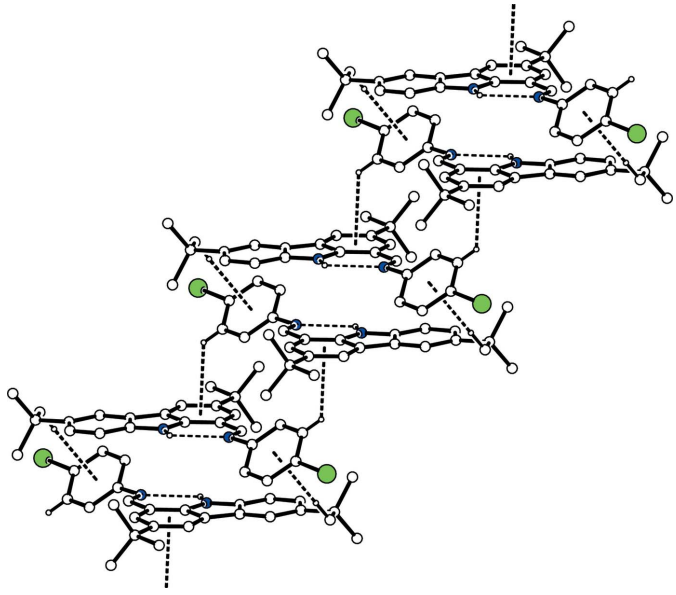


**Figure 2**
A packing diagram of the title compound, showing the ribbon structure. The N—H···N hydrogen bonds and the C—H···$\pi$ interactions are shown as dashed lines. H atoms not involved in the interactions and the minor disorder component have been omitted for clarity.

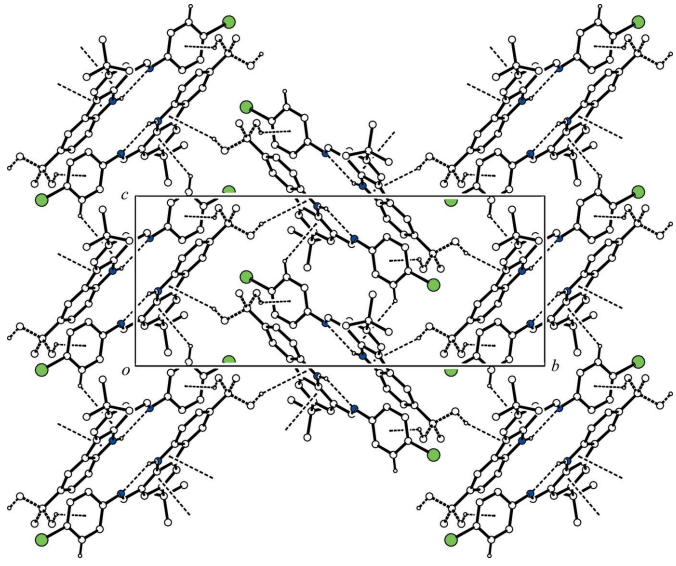



**Figure 3**
A packing diagram of the title compound viewed along the *a* axis, showing a sheet structure. The minor disorder component is shown with bold dashed lines. The N—H···N hydrogen bonds and the C—H···$\pi$ interactions are shown as dashed lines. H atoms not involved in the interactions and the major disorder component have been omitted for clarity.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{27}H_{29}BrN_2$ |
| $M_r$ | 461.42 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 123 |
| $a, b, c$ (Å) | 9.9949 (5), 23.546 (1), 10.2919 (6) |
| $\beta$ (°) | 108.334 (6) |
| $V$ (Å$^3$) | 2299.2 (2) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.80 |
| Crystal size (mm) | 0.40 × 0.30 × 0.20 |
| | |
| Data collection | |
| Diffractometer | Rigaku AFC HyPix-6000 |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018) |
| $T_{min}$, $T_{max}$ | 0.610, 0.696 |
| No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections | 19373, 5268, 4580 |
| $R_{int}$ | 0.025 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.649 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.034, 0.076, 1.03 |
| No. of reflections | 5268 |
| No. of parameters | 312 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.56, −0.54 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SIR92* (Altomare *et al.*, 1993), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *CrystalStructure* (Rigaku, 2016).

(C22*B*—H22*D*···*Cg*3$^{iii}$; *Cg*3 is the centroid of the N3/C4/C5/C11/C10 ring; symmetry code as in Table 1) into a network sheet parallel to (100) (Fig. 3).

## 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40; February 2019; Groom *et al.*, 2016) gave 56 and 5 hits, respectively, for the 3,6-di-*tert*-butyl-9*H*-carbazole and 9*H*-carbazol-1-ylmethylidene fragments. Of these structures, the compounds that resemble the title compound are (3,6-di-tert-butyl-9*H*-carbazole-1,8-diyl)bis[*N*-(naphthalen-1-yl)methanimine] (Nolla-Saltiel *et al.*, 2018) and 1,8-bis[(2,4,6-trimethylphenyl)iminomethyl]-3,6-dimethyl-9*H*-carbazole (Gibson *et al.*, 2003).

## 5. Synthesis and crystallization

3,6-Di-*tert*-butyl-9*H*-carbazole-1-carbaldehyde (154 mg, 0.50 mmol) and 4-bromoaniline (86 mg, 0.50 mmol) were treated in xylene (10 ml) at 423 K under inert gas overnight, followed by evaporation. The recrystallization of the residue from a solvent mixture of acetone and methanol (1:1, *v*:*v*) afforded single crystals of the title compound suitable for X-ray structure analysis (97 mg, 0.21 mmol; yield 42%). $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ = 1.47 [*s*, 9H, $C(CH_3)_3$], 1.49 [*s*, 9H, $C(CH_3)_3$], 7.22 (*td*, 2H, $J_{ortho}$ = 8.6 Hz, $J_{meta}$ = 2.4 Hz, ArH), 7.47–7.58 (*m*, 4H, ArH), 7.67 (*d*, 1H, $J_{meta}$ = 1.8 Hz, ArH), 8.13 (*d*, 1H, $J_{meta}$ = 1.8 Hz, ArH), 8.26 (*d*, 1H, $J_{meta}$ = 1.7 Hz, ArH), 8.72 (*s*, 1H, CH═N), 10.55 (*b*, 1H, NH). HR–MS (*m*/*z*): calculated for $[C_{27}H_{30}BrN_2]^+$, *m*/*z* = 461.1587; found, 461.1627.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atom attached to atom N3 was located in a difference-Fourier map and freely refined. The C-bound H atoms were positioned geometrically (C—H = 0.93–0.96 Å) and refined using a riding model with $U_{iso}$(H) = 1.2$U_{eq}$(C). Orientational disorder of the *tert*-butyl substituent (C20–C23) around the C13—C20 bond axis is observed and the occupancies refined to 0.592 (3) and 0.408 (3).

## Funding information

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# supporting information

*Acta Cryst.* (2019). E**75**, 1429-1431 [https://doi.org/10.1107/S2056989019012374]

# Crystal structure of 4-bromo-*N*-[(3,6-di-*tert*-butyl-9*H*-carbazol-1-yl)methylidene]aniline

**Koji Kubono, Taisuke Matsumoto and Masatsugu Taneda**

## Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2016).

## 4-Bromo-*N*-[(3,6-di-*tert*-butyl-9*H*-carbazol-1-yl)methylidene]aniline

*Crystal data*

$C_{27}H_{29}BrN_2$
$M_r = 461.42$
Monoclinic, $P2_1/c$
$a = 9.9949$ (5) Å
$b = 23.546$ (1) Å
$c = 10.2919$ (6) Å
$\beta = 108.334$ (6)°
$V = 2299.2$ (2) Å$^3$
$Z = 4$
$F(000) = 960.00$
$D_x = 1.333$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 8890 reflections
$\theta = 2.3$–$30.3°$
$\mu = 1.80$ mm$^{-1}$
$T = 123$ K
Prism, yellow
0.40 × 0.30 × 0.20 mm

*Data collection*

Rigaku AFC HyPix-6000 diffractometer
Radiation source: rotating anode X-ray generator, FR-E+
Multi-layer mirror optics monochromator
Detector resolution: 10.0 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2018)
$T_{min} = 0.610$, $T_{max} = 0.696$
19373 measured reflections
5268 independent reflections
4580 reflections with $F^2 > 2.0\sigma(F^2)$
$R_{int} = 0.025$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
$h = -10 \rightarrow 12$
$k = -26 \rightarrow 30$
$l = -13 \rightarrow 13$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.076$
$S = 1.03$
5268 reflections
312 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 1.3852P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.56 e Å$^{-3}$ $\Delta\rho_{min}$ = −0.54 e Å$^{-3}$

*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 was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on $F^2$. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma($F^2$) is used only for calculating R-factor (gt).

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Br1 | 0.32389 (2) | −0.22866 (2) | −0.02368 (2) | 0.04191 (8) | |
| N2 | 0.10884 (14) | −0.03518 (6) | 0.24791 (14) | 0.0214 (3) | |
| N3 | 0.13607 (14) | 0.05539 (6) | 0.44000 (14) | 0.0194 (3) | |
| C4 | −0.00730 (16) | 0.05269 (6) | 0.37843 (15) | 0.0178 (3) | |
| C5 | −0.07237 (16) | 0.09426 (6) | 0.43609 (15) | 0.0171 (3) | |
| C6 | −0.21856 (16) | 0.10061 (7) | 0.38848 (16) | 0.0190 (3) | |
| H6 | −0.2609 | 0.1292 | 0.4243 | 0.023* | |
| C7 | −0.30146 (16) | 0.06474 (7) | 0.28826 (16) | 0.0202 (3) | |
| C8 | −0.23344 (17) | 0.02255 (7) | 0.23600 (16) | 0.0210 (3) | |
| H8 | −0.2887 | −0.0021 | 0.1703 | 0.025* | |
| C9 | −0.08739 (16) | 0.01562 (6) | 0.27729 (16) | 0.0187 (3) | |
| C10 | 0.16594 (16) | 0.09673 (6) | 0.54128 (16) | 0.0183 (3) | |
| C11 | 0.03872 (15) | 0.12215 (6) | 0.54154 (15) | 0.0169 (3) | |
| C12 | 0.03888 (16) | 0.16442 (6) | 0.63623 (15) | 0.0172 (3) | |
| H12 | −0.0456 | 0.1811 | 0.6359 | 0.021* | |
| C13 | 0.16444 (16) | 0.18174 (6) | 0.73110 (15) | 0.0183 (3) | |
| C14 | 0.29004 (16) | 0.15590 (7) | 0.72658 (16) | 0.0213 (3) | |
| H14 | 0.3748 | 0.1675 | 0.7894 | 0.026* | |
| C15 | 0.29330 (16) | 0.11409 (7) | 0.63310 (17) | 0.0216 (3) | |
| H15 | 0.3781 | 0.0982 | 0.6319 | 0.026* | |
| C16 | −0.46276 (17) | 0.06969 (7) | 0.23445 (18) | 0.0249 (4) | |
| C17 | −0.5292 (2) | 0.01470 (9) | 0.2628 (2) | 0.0423 (5) | |
| H17A | −0.5002 | 0.0079 | 0.3597 | 0.051* | |
| H17B | −0.4991 | −0.0163 | 0.2182 | 0.051* | |
| H17C | −0.6300 | 0.0179 | 0.2285 | 0.051* | |
| C18 | −0.5096 (2) | 0.07977 (9) | 0.07942 (19) | 0.0351 (4) | |
| H18A | −0.6106 | 0.0811 | 0.0447 | 0.042* | |
| H18B | −0.4758 | 0.0494 | 0.0359 | 0.042* | |
| H18C | −0.4716 | 0.1152 | 0.0606 | 0.042* | |
| C19 | −0.51743 (19) | 0.11897 (9) | 0.2992 (2) | 0.0386 (5) | |
| H19A | −0.4766 | 0.1538 | 0.2812 | 0.046* | |
| H19B | −0.4920 | 0.1132 | 0.3963 | 0.046* | |
| H19C | −0.6182 | 0.1210 | 0.2610 | 0.046* | |
| C20 | 0.16630 (17) | 0.22683 (7) | 0.83868 (17) | 0.0226 (3) | |
| C21A | 0.2398 (4) | 0.20070 (14) | 0.9822 (3) | 0.0349 (8) | 0.592 (3) |

| | | | | | |
|---|---|---|---|---|---|
| H21A | 0.2411 | 0.2281 | 1.0517 | 0.042* | 0.592 (3) |
| H21B | 0.3347 | 0.1903 | 0.9893 | 0.042* | 0.592 (3) |
| H21C | 0.1890 | 0.1676 | 0.9943 | 0.042* | 0.592 (3) |
| C22A | 0.0240 (4) | 0.24682 (17) | 0.8322 (4) | 0.0458 (11) | 0.592 (3) |
| H22A | −0.0202 | 0.2644 | 0.7452 | 0.055* | 0.592 (3) |
| H22B | 0.0317 | 0.2739 | 0.9040 | 0.055* | 0.592 (3) |
| H22C | −0.0318 | 0.2151 | 0.8434 | 0.055* | 0.592 (3) |
| C23A | 0.2585 (4) | 0.27633 (13) | 0.8214 (3) | 0.0344 (8) | 0.592 (3) |
| H23A | 0.2170 | 0.2935 | 0.7333 | 0.041* | 0.592 (3) |
| H23B | 0.3509 | 0.2625 | 0.8284 | 0.041* | 0.592 (3) |
| H23C | 0.2655 | 0.3040 | 0.8917 | 0.041* | 0.592 (3) |
| C21B | 0.0816 (5) | 0.2036 (2) | 0.9295 (4) | 0.0310 (11) | 0.408 (3) |
| H21D | 0.1277 | 0.1705 | 0.9775 | 0.037* | 0.408 (3) |
| H21E | −0.0118 | 0.1937 | 0.8731 | 0.037* | 0.408 (3) |
| H21F | 0.0762 | 0.2321 | 0.9943 | 0.037* | 0.408 (3) |
| C22B | 0.0843 (5) | 0.28167 (19) | 0.7672 (5) | 0.0324 (11) | 0.408 (3) |
| H22D | 0.0760 | 0.3078 | 0.8359 | 0.039* | 0.408 (3) |
| H22E | −0.0080 | 0.2711 | 0.7094 | 0.039* | 0.408 (3) |
| H22F | 0.1351 | 0.2994 | 0.7130 | 0.039* | 0.408 (3) |
| C23B | 0.3089 (4) | 0.2460 (2) | 0.9280 (5) | 0.0346 (12) | 0.408 (3) |
| H23D | 0.3601 | 0.2140 | 0.9772 | 0.041* | 0.408 (3) |
| H23E | 0.2979 | 0.2739 | 0.9917 | 0.041* | 0.408 (3) |
| H23F | 0.3599 | 0.2622 | 0.8721 | 0.041* | 0.408 (3) |
| C24 | −0.02473 (16) | −0.02866 (7) | 0.21740 (16) | 0.0197 (3) | |
| H24 | −0.0838 | −0.0533 | 0.1544 | 0.024* | |
| C25 | 0.15800 (17) | −0.07912 (7) | 0.18052 (16) | 0.0207 (3) | |
| C26 | 0.26499 (17) | −0.11434 (7) | 0.25860 (18) | 0.0235 (3) | |
| H26 | 0.3037 | −0.1079 | 0.3521 | 0.028* | |
| C27 | 0.31439 (17) | −0.15892 (7) | 0.19842 (19) | 0.0263 (4) | |
| H27 | 0.3834 | −0.1833 | 0.2514 | 0.032* | |
| C28 | 0.25953 (18) | −0.16661 (7) | 0.05853 (19) | 0.0263 (4) | |
| C29 | 0.15945 (19) | −0.13042 (8) | −0.02231 (19) | 0.0288 (4) | |
| H29 | 0.1269 | −0.1351 | −0.1168 | 0.035* | |
| C30 | 0.10778 (18) | −0.08681 (7) | 0.03954 (17) | 0.0261 (4) | |
| H30 | 0.0389 | −0.0625 | −0.0140 | 0.031* | |
| H3 | 0.187 (2) | 0.0341 (9) | 0.426 (2) | 0.027 (5)* | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.03992 (12) | 0.03025 (11) | 0.05975 (15) | 0.00525 (8) | 0.02168 (10) | −0.01567 (9) |
| N2 | 0.0257 (7) | 0.0183 (6) | 0.0222 (7) | −0.0004 (5) | 0.0103 (6) | −0.0001 (5) |
| N3 | 0.0172 (6) | 0.0193 (7) | 0.0222 (7) | 0.0024 (5) | 0.0069 (5) | −0.0017 (5) |
| C4 | 0.0192 (7) | 0.0168 (7) | 0.0181 (7) | 0.0000 (6) | 0.0066 (6) | 0.0036 (6) |
| C5 | 0.0208 (7) | 0.0157 (7) | 0.0154 (7) | −0.0007 (6) | 0.0065 (6) | 0.0015 (6) |
| C6 | 0.0196 (7) | 0.0182 (7) | 0.0194 (8) | 0.0025 (6) | 0.0065 (6) | 0.0007 (6) |
| C7 | 0.0185 (8) | 0.0211 (8) | 0.0198 (8) | 0.0005 (6) | 0.0045 (6) | 0.0009 (6) |
| C8 | 0.0229 (8) | 0.0183 (7) | 0.0202 (8) | −0.0021 (6) | 0.0045 (6) | −0.0017 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C9 | 0.0225 (8) | 0.0161 (7) | 0.0188 (7) | 0.0000 (6) | 0.0082 (6) | 0.0016 (6) |
| C10 | 0.0214 (8) | 0.0160 (7) | 0.0186 (7) | 0.0009 (6) | 0.0078 (6) | 0.0021 (6) |
| C11 | 0.0166 (7) | 0.0165 (7) | 0.0175 (7) | −0.0006 (6) | 0.0053 (6) | 0.0035 (6) |
| C12 | 0.0163 (7) | 0.0166 (7) | 0.0193 (7) | 0.0007 (6) | 0.0063 (6) | 0.0020 (6) |
| C13 | 0.0200 (7) | 0.0178 (7) | 0.0178 (7) | −0.0018 (6) | 0.0068 (6) | 0.0018 (6) |
| C14 | 0.0164 (7) | 0.0246 (8) | 0.0207 (8) | −0.0023 (6) | 0.0025 (6) | 0.0006 (6) |
| C15 | 0.0159 (7) | 0.0234 (8) | 0.0258 (8) | 0.0029 (6) | 0.0067 (6) | 0.0020 (7) |
| C16 | 0.0175 (8) | 0.0246 (8) | 0.0291 (9) | −0.0008 (6) | 0.0023 (7) | −0.0044 (7) |
| C17 | 0.0228 (9) | 0.0388 (11) | 0.0652 (14) | −0.0008 (8) | 0.0135 (9) | 0.0078 (10) |
| C18 | 0.0256 (9) | 0.0400 (11) | 0.0324 (10) | 0.0030 (8) | −0.0013 (8) | −0.0039 (8) |
| C19 | 0.0195 (8) | 0.0479 (12) | 0.0426 (11) | 0.0070 (8) | 0.0017 (8) | −0.0161 (9) |
| C20 | 0.0229 (8) | 0.0219 (8) | 0.0220 (8) | −0.0047 (6) | 0.0058 (6) | −0.0037 (6) |
| C21A | 0.049 (2) | 0.0336 (17) | 0.0241 (16) | −0.0039 (14) | 0.0149 (14) | −0.0042 (13) |
| C22A | 0.0303 (17) | 0.047 (2) | 0.054 (2) | 0.0007 (15) | 0.0055 (16) | −0.0364 (19) |
| C23A | 0.0448 (19) | 0.0241 (15) | 0.0292 (17) | −0.0123 (13) | 0.0045 (14) | −0.0049 (13) |
| C21B | 0.039 (3) | 0.035 (2) | 0.021 (2) | −0.012 (2) | 0.0112 (19) | −0.0070 (18) |
| C22B | 0.045 (3) | 0.026 (2) | 0.026 (2) | 0.0088 (19) | 0.012 (2) | −0.0038 (18) |
| C23B | 0.021 (2) | 0.038 (3) | 0.043 (3) | −0.0064 (18) | 0.006 (2) | −0.016 (2) |
| C24 | 0.0243 (8) | 0.0169 (7) | 0.0179 (7) | −0.0011 (6) | 0.0066 (6) | 0.0000 (6) |
| C25 | 0.0229 (8) | 0.0171 (7) | 0.0248 (8) | −0.0020 (6) | 0.0114 (7) | −0.0019 (6) |
| C26 | 0.0199 (8) | 0.0268 (8) | 0.0244 (8) | −0.0016 (6) | 0.0080 (7) | −0.0007 (7) |
| C27 | 0.0202 (8) | 0.0238 (8) | 0.0368 (10) | 0.0024 (6) | 0.0117 (7) | 0.0028 (7) |
| C28 | 0.0258 (8) | 0.0194 (8) | 0.0389 (10) | −0.0004 (6) | 0.0175 (8) | −0.0067 (7) |
| C29 | 0.0342 (9) | 0.0286 (9) | 0.0244 (9) | 0.0021 (7) | 0.0104 (7) | −0.0050 (7) |
| C30 | 0.0306 (9) | 0.0232 (8) | 0.0244 (9) | 0.0054 (7) | 0.0084 (7) | 0.0016 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C28 | 1.8992 (16) | C19—H19B | 0.9600 |
| N2—C24 | 1.281 (2) | C19—H19C | 0.9600 |
| N2—C25 | 1.417 (2) | C20—C22A | 1.479 (4) |
| N3—C4 | 1.374 (2) | C20—C23B | 1.502 (4) |
| N3—C10 | 1.388 (2) | C20—C23A | 1.530 (3) |
| N3—H3 | 0.76 (2) | C20—C21B | 1.545 (5) |
| C4—C9 | 1.401 (2) | C20—C21A | 1.555 (4) |
| C4—C5 | 1.406 (2) | C20—C22B | 1.581 (5) |
| C5—C6 | 1.395 (2) | C21A—H21A | 0.9600 |
| C5—C11 | 1.444 (2) | C21A—H21B | 0.9600 |
| C6—C7 | 1.388 (2) | C21A—H21C | 0.9600 |
| C6—H6 | 0.9300 | C22A—H22A | 0.9600 |
| C7—C8 | 1.403 (2) | C22A—H22B | 0.9600 |
| C7—C16 | 1.535 (2) | C22A—H22C | 0.9600 |
| C8—C9 | 1.396 (2) | C23A—H23A | 0.9600 |
| C8—H8 | 0.9300 | C23A—H23B | 0.9600 |
| C9—C24 | 1.450 (2) | C23A—H23C | 0.9600 |
| C10—C15 | 1.387 (2) | C21B—H21D | 0.9600 |
| C10—C11 | 1.406 (2) | C21B—H21E | 0.9600 |
| C11—C12 | 1.393 (2) | C21B—H21F | 0.9600 |

| | | | |
|---|---|---|---|
| C12—C13 | 1.387 (2) | C22B—H22D | 0.9600 |
| C12—H12 | 0.9300 | C22B—H22E | 0.9600 |
| C13—C14 | 1.409 (2) | C22B—H22F | 0.9600 |
| C13—C20 | 1.530 (2) | C23B—H23D | 0.9600 |
| C14—C15 | 1.384 (2) | C23B—H23E | 0.9600 |
| C14—H14 | 0.9300 | C23B—H23F | 0.9600 |
| C15—H15 | 0.9300 | C24—H24 | 0.9300 |
| C16—C19 | 1.523 (2) | C25—C30 | 1.390 (2) |
| C16—C17 | 1.525 (3) | C25—C26 | 1.392 (2) |
| C16—C18 | 1.533 (3) | C26—C27 | 1.386 (2) |
| C17—H17A | 0.9600 | C26—H26 | 0.9300 |
| C17—H17B | 0.9600 | C27—C28 | 1.382 (3) |
| C17—H17C | 0.9600 | C27—H27 | 0.9300 |
| C18—H18A | 0.9600 | C28—C29 | 1.377 (3) |
| C18—H18B | 0.9600 | C29—C30 | 1.390 (2) |
| C18—H18C | 0.9600 | C29—H29 | 0.9300 |
| C19—H19A | 0.9600 | C30—H30 | 0.9300 |

| | | | |
|---|---|---|---|
| C24—N2—C25 | 117.55 (14) | C13—C20—C23A | 108.37 (17) |
| C4—N3—C10 | 108.99 (13) | C23B—C20—C21B | 109.3 (3) |
| C4—N3—H3 | 123.0 (15) | C13—C20—C21B | 107.9 (2) |
| C10—N3—H3 | 127.4 (15) | C22A—C20—C21A | 109.2 (2) |
| N3—C4—C9 | 129.86 (14) | C13—C20—C21A | 107.92 (17) |
| N3—C4—C5 | 109.09 (13) | C23A—C20—C21A | 106.8 (2) |
| C9—C4—C5 | 121.03 (14) | C23B—C20—C22B | 107.0 (3) |
| C6—C5—C4 | 119.92 (14) | C13—C20—C22B | 110.1 (2) |
| C6—C5—C11 | 133.48 (14) | C21B—C20—C22B | 105.5 (3) |
| C4—C5—C11 | 106.59 (13) | C20—C21A—H21A | 109.5 |
| C7—C6—C5 | 120.68 (14) | C20—C21A—H21B | 109.5 |
| C7—C6—H6 | 119.7 | H21A—C21A—H21B | 109.5 |
| C5—C6—H6 | 119.7 | C20—C21A—H21C | 109.5 |
| C6—C7—C8 | 117.89 (14) | H21A—C21A—H21C | 109.5 |
| C6—C7—C16 | 122.38 (14) | H21B—C21A—H21C | 109.5 |
| C8—C7—C16 | 119.73 (14) | C20—C22A—H22A | 109.5 |
| C9—C8—C7 | 123.55 (15) | C20—C22A—H22B | 109.5 |
| C9—C8—H8 | 118.2 | H22A—C22A—H22B | 109.5 |
| C7—C8—H8 | 118.2 | C20—C22A—H22C | 109.5 |
| C8—C9—C4 | 116.87 (14) | H22A—C22A—H22C | 109.5 |
| C8—C9—C24 | 120.32 (14) | H22B—C22A—H22C | 109.5 |
| C4—C9—C24 | 122.80 (14) | C20—C23A—H23A | 109.5 |
| C15—C10—N3 | 130.74 (14) | C20—C23A—H23B | 109.5 |
| C15—C10—C11 | 120.66 (14) | H23A—C23A—H23B | 109.5 |
| N3—C10—C11 | 108.59 (13) | C20—C23A—H23C | 109.5 |
| C12—C11—C10 | 120.24 (14) | H23A—C23A—H23C | 109.5 |
| C12—C11—C5 | 133.04 (14) | H23B—C23A—H23C | 109.5 |
| C10—C11—C5 | 106.69 (13) | C20—C21B—H21D | 109.5 |
| C13—C12—C11 | 120.29 (14) | C20—C21B—H21E | 109.5 |
| C13—C12—H12 | 119.9 | H21D—C21B—H21E | 109.5 |

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|---|---|---|---|
| C11—C12—H12 | 119.9 | C20—C21B—H21F | 109.5 |
| C12—C13—C14 | 117.91 (14) | H21D—C21B—H21F | 109.5 |
| C12—C13—C20 | 121.06 (14) | H21E—C21B—H21F | 109.5 |
| C14—C13—C20 | 121.03 (14) | C20—C22B—H22D | 109.5 |
| C15—C14—C13 | 123.11 (14) | C20—C22B—H22E | 109.5 |
| C15—C14—H14 | 118.4 | H22D—C22B—H22E | 109.5 |
| C13—C14—H14 | 118.4 | C20—C22B—H22F | 109.5 |
| C14—C15—C10 | 117.77 (14) | H22D—C22B—H22F | 109.5 |
| C14—C15—H15 | 121.1 | H22E—C22B—H22F | 109.5 |
| C10—C15—H15 | 121.1 | C20—C23B—H23D | 109.5 |
| C19—C16—C17 | 109.00 (16) | C20—C23B—H23E | 109.5 |
| C19—C16—C18 | 107.66 (15) | H23D—C23B—H23E | 109.5 |
| C17—C16—C18 | 108.79 (15) | C20—C23B—H23F | 109.5 |
| C19—C16—C7 | 112.37 (14) | H23D—C23B—H23F | 109.5 |
| C17—C16—C7 | 109.72 (14) | H23E—C23B—H23F | 109.5 |
| C18—C16—C7 | 109.22 (14) | N2—C24—C9 | 122.55 (15) |
| C16—C17—H17A | 109.5 | N2—C24—H24 | 118.7 |
| C16—C17—H17B | 109.5 | C9—C24—H24 | 118.7 |
| H17A—C17—H17B | 109.5 | C30—C25—C26 | 119.00 (15) |
| C16—C17—H17C | 109.5 | C30—C25—N2 | 122.63 (15) |
| H17A—C17—H17C | 109.5 | C26—C25—N2 | 118.32 (14) |
| H17B—C17—H17C | 109.5 | C27—C26—C25 | 120.68 (16) |
| C16—C18—H18A | 109.5 | C27—C26—H26 | 119.7 |
| C16—C18—H18B | 109.5 | C25—C26—H26 | 119.7 |
| H18A—C18—H18B | 109.5 | C28—C27—C26 | 118.97 (16) |
| C16—C18—H18C | 109.5 | C28—C27—H27 | 120.5 |
| H18A—C18—H18C | 109.5 | C26—C27—H27 | 120.5 |
| H18B—C18—H18C | 109.5 | C29—C28—C27 | 121.56 (15) |
| C16—C19—H19A | 109.5 | C29—C28—Br1 | 119.37 (14) |
| C16—C19—H19B | 109.5 | C27—C28—Br1 | 119.07 (13) |
| H19A—C19—H19B | 109.5 | C28—C29—C30 | 118.97 (16) |
| C16—C19—H19C | 109.5 | C28—C29—H29 | 120.5 |
| H19A—C19—H19C | 109.5 | C30—C29—H29 | 120.5 |
| H19B—C19—H19C | 109.5 | C25—C30—C29 | 120.66 (16) |
| C22A—C20—C13 | 113.32 (17) | C25—C30—H30 | 119.7 |
| C23B—C20—C13 | 116.4 (2) | C29—C30—H30 | 119.7 |
| C22A—C20—C23A | 111.0 (2) | | |

| | | | |
|---|---|---|---|
| C10—N3—C4—C9 | −175.87 (15) | N3—C10—C15—C14 | −178.10 (16) |
| C10—N3—C4—C5 | 2.32 (17) | C11—C10—C15—C14 | 1.7 (2) |
| N3—C4—C5—C6 | 178.89 (13) | C6—C7—C16—C19 | 2.2 (2) |
| C9—C4—C5—C6 | −2.7 (2) | C8—C7—C16—C19 | −178.06 (16) |
| N3—C4—C5—C11 | −1.96 (16) | C6—C7—C16—C17 | −119.19 (18) |
| C9—C4—C5—C11 | 176.41 (14) | C8—C7—C16—C17 | 60.5 (2) |
| C4—C5—C6—C7 | 2.6 (2) | C6—C7—C16—C18 | 121.64 (17) |
| C11—C5—C6—C7 | −176.26 (16) | C8—C7—C16—C18 | −58.7 (2) |
| C5—C6—C7—C8 | −0.6 (2) | C12—C13—C20—C22A | 2.2 (3) |
| C5—C6—C7—C16 | 179.10 (14) | C14—C13—C20—C22A | −176.9 (2) |

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|---|---|---|---|
| C6—C7—C8—C9 | −1.4 (2) | C12—C13—C20—C23B | −174.8 (3) |
| C16—C7—C8—C9 | 178.89 (15) | C14—C13—C20—C23B | 6.2 (3) |
| C7—C8—C9—C4 | 1.3 (2) | C12—C13—C20—C23A | −121.4 (2) |
| C7—C8—C9—C24 | −179.34 (15) | C14—C13—C20—C23A | 59.5 (2) |
| N3—C4—C9—C8 | 178.81 (15) | C12—C13—C20—C21B | 61.9 (3) |
| C5—C4—C9—C8 | 0.8 (2) | C14—C13—C20—C21B | −117.1 (2) |
| N3—C4—C9—C24 | −0.6 (3) | C12—C13—C20—C21A | 123.2 (2) |
| C5—C4—C9—C24 | −178.55 (14) | C14—C13—C20—C21A | −55.9 (2) |
| C4—N3—C10—C15 | 178.11 (16) | C12—C13—C20—C22B | −52.8 (3) |
| C4—N3—C10—C11 | −1.74 (17) | C14—C13—C20—C22B | 128.1 (2) |
| C15—C10—C11—C12 | −1.3 (2) | C25—N2—C24—C9 | −178.58 (14) |
| N3—C10—C11—C12 | 178.55 (13) | C8—C9—C24—N2 | 177.08 (15) |
| C15—C10—C11—C5 | −179.37 (14) | C4—C9—C24—N2 | −3.6 (2) |
| N3—C10—C11—C5 | 0.50 (17) | C24—N2—C25—C30 | 48.4 (2) |
| C6—C5—C11—C12 | 2.2 (3) | C24—N2—C25—C26 | −134.37 (16) |
| C4—C5—C11—C12 | −176.82 (16) | C30—C25—C26—C27 | −4.4 (2) |
| C6—C5—C11—C10 | 179.87 (16) | N2—C25—C26—C27 | 178.28 (14) |
| C4—C5—C11—C10 | 0.88 (16) | C25—C26—C27—C28 | 2.5 (2) |
| C10—C11—C12—C13 | −0.1 (2) | C26—C27—C28—C29 | 1.3 (3) |
| C5—C11—C12—C13 | 177.38 (15) | C26—C27—C28—Br1 | −178.58 (12) |
| C11—C12—C13—C14 | 0.9 (2) | C27—C28—C29—C30 | −3.1 (3) |
| C11—C12—C13—C20 | −178.14 (14) | Br1—C28—C29—C30 | 176.80 (13) |
| C12—C13—C14—C15 | −0.5 (2) | C26—C25—C30—C29 | 2.5 (3) |
| C20—C13—C14—C15 | 178.59 (15) | N2—C25—C30—C29 | 179.78 (15) |
| C13—C14—C15—C10 | −0.8 (2) | C28—C29—C30—C25 | 1.1 (3) |

*Hydrogen-bond geometry (Å, º)*

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the C25–C30, C4–C9 and N3/C4/C5/C11/C10 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···N2 | 0.76 (2) | 2.39 (2) | 2.862 (2) | 121.3 (16) |
| C22*A*—H22*C*···*Cg*1$^{i}$ | 0.96 | 2.92 | 3.878 (4) | 177 |
| C29—H29···*Cg*2$^{ii}$ | 0.93 | 2.95 | 3.613 (2) | 129 |
| C21*B*—H21*E*···*Cg*1$^{i}$ | 0.96 | 2.62 | 3.391 (5) | 138 |
| C22*B*—H22*D*···*Cg*3$^{iii}$ | 0.96 | 2.92 | 3.839 (5) | 159 |

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