# Synthesis and crystal structure of 2,9-diamino-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene

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The *cis*- form of diaminodibenzocyclooctane (DADBCO, $C_{16}H_{18}N_2$) is of interest as a negative coefficient of thermal expansion (CTE) material. The crystal structure was determined through single-crystal X-ray diffraction at 100 K and is presented herein.

## 1. Chemical context

Thermoset polymers are high performance materials that demonstrate excellent chemical, thermal, and mechanical stability at low weight and cost, making them ubiquitous in a wide range of applications such as insulating layers, encapsulants, adhesives, barriers, and composites (Biron, 2013; Brostow *et al.*, 2014; Dickie *et al.*, 1988; Pascault *et al.*, 2002; Guo, 2018). Because these applications involve an interface between different materials, the thermal expansion behaviors of each constituent must be considered to achieve suitable performance. Most solid materials exhibit a positive coefficient of thermal expansion (CTE), the rate at which thermal expansion occurs during positive temperature change. Large differences in CTE between the various materials in composites and devices results in internal thermomechanical stress at interfaces, which in turn reduces service life and may initiate device failure (Okura *et al.*, 2000; de Vreugd *et al.*, 2010).
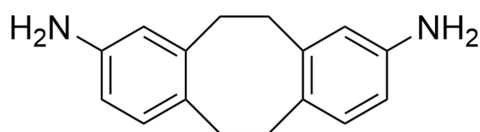


One strategy to mitigate CTE incompatibilities is the covalent incorporation of thermally activated contractile units into the polymer (Shen *et al.*, 2013). These units counteract the thermal expansion during heating, reducing the CTE below that of the parent material. Materials capable of zero or even negative CTE are achievable with this method. Dibenzocyclooctane (DBCO) is one such unit, which achieves a thermally activated volume decrease by undergoing a reversible twist-boat to chair conformational change (Shen *et al.*, 2013; Wang *et al.*, 2018; Fu *et al.*, 2020). Diaminodibenzocyclooctane (DADBCO), an aminated derivative, is also able to undergo this CTE modifying conformational change. However, it was found that epoxy resins incorporating 2,2′-DADBCO (*cis*) demonstrated negative CTE behavior while those utilizing 2,3′-DADBCO (*trans*) did not (Foster *et al.*, 2021). These two materials are not differentiable by most characterization methods including IR, MS, and NMR. In addition, melting
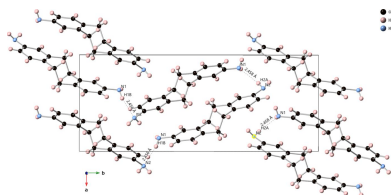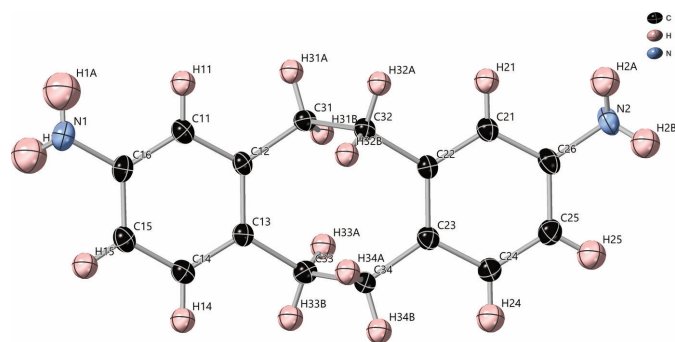
**Figure 1**
Displacement ellipsoid plot of *cis*-DADBCO with atom labels. Ellipsoids are drawn at the 50% probability level.

points are unreliable due to the difficulty of separation of these two isomers.

## 2. Structural Commentary

The *cis*-DADBCO molecules (point group $C2$) crystallizes in the chair conformation in space group $Pna2_1$. The structure was determined at 100 K and is illustrated in Fig. 1. The carbon rings are labeled as Ring 1: C11–C16 with nitrogen N1 connected to Ring 1 at C16, Ring 2: C21–C26 with N2 connected to Ring 2 at C26. The center cyclooctane contains carbon atoms: C12, C13, C31–C34, C22, C23. The plane of Ring 1 (C11–C16) makes a 59.9 (1)° angle with the plane that contains the four central atoms of the chair cyclooctane, C31–34. Nitrogen N1 is essentially planar with Ring 1 with a deviation from the plane of −0.025 (4) Å. The plane of Ring 2 (C21–26) makes a 56.7 (1)° angle with the aforementioned cyclooctane plane. Nitrogen N2 is essentially planar with Ring 2 with a deviation from the plane of 0.026 (4)°. The puckering parameters (Cremer & Pople, 1975) of the center cyclooctane are: total puckering amplitude $Q = 0.906$ (4) Å, $q_2 = 0.024$ (4) Å $\varphi_2 = 146$ (9)°, $q_3 = 0.906$ (4) Å $\varphi_3 = 111.6$ (2)°, $q_4 = -0.005$ (4) Å.

## 3. Supramolecular Features

Hydrogen bonding appears to be possible between the two amine groups from one independent molecule to the next
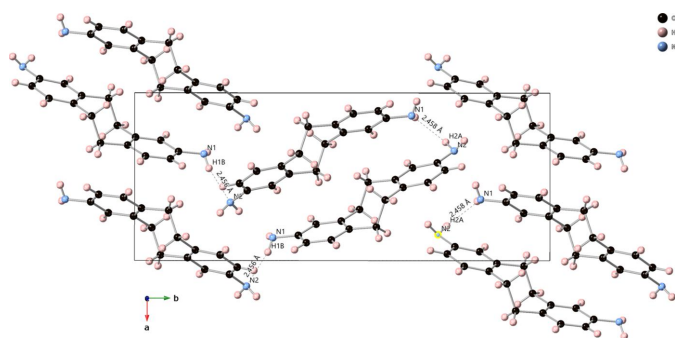


**Figure 2**
Hydrogen bonding in the crystal packing of the title compound. Incomplete molecules in the range are omitted for clarity. Displacement ellipsoids are drawn at 50% probability.

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

$Cg1$ and $Cg2$ are the centroids of rings C11–C16 and C21–C26, respectively.

| $D-\mathrm{H}\cdots A$ | $D-\mathrm{H}$ | $\mathrm{H}\cdots A$ | $D\cdots A$ | $D-\mathrm{H}\cdots A$ |
|---|---|---|---|---|
| N1—H1$B$···N2$^i$ | 0.86 (4) | 2.46 (4) | 3.295 (5) | 165 (4) |
| N2—H2$A$···N1$^{ii}$ | 0.88 | 2.46 | 3.295 (5) | 159 |
| N2—H2$B$···$Cg2^{iii}$ | 0.88 | 2.96 | 3.742 (4) | 149 |
| C14—H14···$Cg1^{iv}$ | 0.95 | 2.84 | 3.572 (4) | 135 |
| C32—H32$A$···$Cg1^{ii}$ | 0.99 | 2.78 | 3.640 (4) | 145 |

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

through hydrogen H1$B$ on nitrogen N2 to nitrogen N1 (bond length 2.452 Å) and through hydrogen H2$A$ on nitrogen N2 to nitrogen N1 (bond length 2.458 Å). This information is summarized in Table 1 and illustrated in Fig. 2. N—H..$\pi$ and C—H..$\pi$ interactions are also included in Table 1.

## 4. Database survey

A search was performed on the Cambridge Structural Database (CSD Version 5.45, March 2024; Groom *et al.*, 2016) using ConQuest (Version 2024.1.0), and this aminated structure was not found. At time of submission there were eight 6,8,6 ring system entries in the CSD, with cyclooctane as the central ring, no additional rings linked, and no chemical substitutions in the core 6,8,6 carbon rings. A search of the chemical formula also yielded no results. An overview of 6,8,6 ring systems can be found in Domiano *et al.* (1992). The 6,8,6 motif also appears in circulene systems, see Miyoshi *et al.* (2022).

## 5. Synthesis and crystallization

### Synthesis of dibenzocyclooctane (DBCO)

The synthesis of DBCO was carried out according to a literature procedure (Franck *et al.*, 2012). An oven-dried three-necked round-bottom flask equipped with a stir bar was charged with lithium metal (3.30 g, 478 mmol, 2.5 equiv) and 100 mL of anhydrous THF in an Ar-filled glovebox. The flask was sealed with two rubber septa and vacuum adapter with a stopcock. The flask was removed from the glovebox and connected to a Schlenk line. The flask was fitted with a reflux condenser and pressure-equalizing addition funnel under $N_2$ flow. A solution of $\alpha,\alpha'$-dibromo-*o*-xylene (50.2 g, 190 mmol, 1 equiv) in 100 mL of anhydrous THF was prepared and transferred to the addition funnel. This solution was added dropwise to the Li suspension with vigorous stirring under an $N_2$ atmosphere. After ~1/4 of this solution had been added, the reaction mixture began to reflux, and the addition was paused to allow the exotherm to subside. After 5 min, the dropwise addition was resumed, taking 1 h to add the remaining solution. The addition funnel was replaced with a glass stopper and the reaction mixture was heated at reflux overnight under $N_2$. Complete consumption of the starting material was confirmed by TLC in petroleum ether. The reaction flask was cooled in an ice bath and the reaction mixture was then carefully filtered over a glass frit to remove unreacted Li. The filtrate was concentrated *in vacuo* and was

re-suspended in 200 mL of $CH_2Cl_2$. The resulting suspension was filtered over a pad of silica gel and the silica gel pad was washed with an additional 200 mL of $CH_2Cl_2$. The combined filtrates were dried over $Na_2SO_4$ and concentrated *in vacuo*, yielding 20.7 g of viscous yellow oil that solidified upon standing. The crude product was further purified *via* Kugel-rohr distillation at 463 K under vacuum to afford the pure product as a white crystalline solid.

### Synthesis of dinitro dibenzocyclooctane (DNDBCO)

DBCO (4.55 g, 21.9 mmol, 1 equiv) was dissolved in 200 mL of $CH_2Cl_2$ in a round-bottom flask equipped with a stir bar. The flask was fitted with a pressure-equalizing addition funnel and was placed in an ice bath. To the flask was added 25 mL $HNO_3$ (~20 equiv) dropwise *via* the addition funnel at 273 K. During the addition, the reaction mixture developed a deep red color. The flask was removed from the ice bath and allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 2 h, during which time the color of the reaction mixture changed from deep red to yellow–orange. The reaction mixture was poured into a beaker containing 300 mL of cold deionized (DI) $H_2O$ to quench the reaction, and this biphasic mixture was transferred to a separatory funnel. The aqueous layer was discarded, and the organic layer was washed subsequently with DI $H_2O$, saturated $NaHCO_3$ solution ($2\times$), and brine, dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. Upon further drying under vacuum, a yellow solid was obtained that was used in the next step without further purification.

### Synthesis of diamino dibenzocyclooctane (DADBCO)

A three-necked round-bottom flask equipped with a stir bar was charged with 10% Pd/C (0.89 g, 5 mol% Pd relative to DNDBCO). The flask was fitted with two rubber septa and a vacuum adapter and was placed under an $N_2$ atmosphere. To the flask was added 150 mL of MeOH followed by DNDBCO (5.05 g, 16.9 mmol, 1 equiv) under $N_2$ flow. The rubber septa were replaced with vacuum adapters attached to $H_2$-filled balloons, and the $N_2$ atmosphere was exchanged for $H_2$ *via* five vacuum/$H_2$-back-fill cycles. The reaction mixture was then stirred overnight at room temperature under $H_2$, over which time the solid DNDBCO slowly dissolved. The complete consumption of the starting material was confirmed by TLC in 2:1 hexane/ethyl acetate. The reaction mixture was filtered over a pad of celite to remove the Pd/C and the filtrate was concentrated *in vacuo*. The resulting dark-red oil was re-dissolved in $1M$ HCl solution and was washed with $CH_2Cl_2$ ($3\times$). The pH of the solution was then adjusted to pH >10 using ~$4M$ NaOH solution, and the precipitated product was extracted with EtOAc ($2\times$). The combined EtOAc solutions were washed with DI $H_2O$ and brine, dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. Further drying under vacuum afforded the product as a light-pink solid (3.05 g, 76% yield). Note: DADBCO was obtained as a mixture of isomers, where the ratio of *ortho*/*meta* anilines was ~2:3. The various isomers could be isolated *via* exhaustive silica gel chromatography, eluting with a gradient from 0–50% EtOAc in hexane. In particular, the 2,2′ and 2,3′ isomers were suspected as the last and second to last compounds that eluted from the

**Table 2**
Experimental details.

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | $C_{16}H_{18}N_2$ |
| $M_r$ | 238.32 |
| Crystal system, space group | Orthorhombic, $Pna2_1$ |
| Temperature (K) | 100 |
| $a, b, c$ (Å) | 8.8641 (3), 22.0075 (6), 6.2771 (2) |
| $V$ (Å$^3$) | 1224.52 (7) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.59 |
| Crystal size (mm) | $0.1 \times 0.1 \times 0.01$ |
| | |
| **Data collection** | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Krause *et al.*, 2015) |
| $T_{min}$, $T_{max}$ | 0.459, 0.754 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 39813, 2060, 1781 |
| $R_{int}$ | 0.118 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.588 |
| | |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.046, 0.106, 1.08 |
| No. of reflections | 2060 |
| No. of parameters | 173 |
| No. of restraints | 172 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.18, −0.22 |
| Absolute structure | Refined as an inversion twin |
| Absolute structure parameter | 0.3 (12) |

Computer programs: *APEX2* and *SAINT* (Bruker, 2019), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

column, respectively. A suitable crystal of the 2,2′ material was grown for XRD analysis by allowing a saturated hot toluene solution to cool to room temperature over several hours followed by further cooling to 273 K.

## 6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2. The hydrogen atoms on N2 were placed with a riding-bond model, whereas the hydrogen atoms on N1 were placed manually to match observed electron density. The distance of the manually placed atoms was constrained with DFIX and for the hydrogen atoms on N1 the isotropic thermal parameters were refined without constraints. All other H atoms were generated *via* the riding-bond model and refined with $U(H) = 1.2U_{eq}(C/N)$. The absolute structure was not determined due to the absence of heavy atoms (Flack parameter = 0.3), and the inversion twin law was used for refinement.

## Acknowledgements

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## Synthesis and crystal structure of 2,9-diamino-5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene

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**Computing details**

**2,9-Diamino-5,6,11,12-tetrahydrodibenzo[a,e][8]annulene**

*Crystal data*

| | |
|---|---|
| $C_{16}H_{18}N_2$ | $D_x = 1.293$ Mg m$^{-3}$ |
| $M_r = 238.32$ | Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å |
| Orthorhombic, $Pna2_1$ | Cell parameters from 8510 reflections |
| $a = 8.8641$ (3) Å | $\theta = 4.0$–73.6° |
| $b = 22.0075$ (6) Å | $\mu = 0.59$ mm$^{-1}$ |
| $c = 6.2771$ (2) Å | $T = 100$ K |
| $V = 1224.52$ (7) Å$^3$ | Needle, clear light green |
| $Z = 4$ | $0.1 \times 0.1 \times 0.01$ mm |
| $F(000) = 512$ | |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD diffractometer | 2060 independent reflections |
| | 1781 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.118$ |
| Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015) | $\theta_{max} = 65.0°$, $\theta_{min} = 4.0°$ |
| | $h = -10 \rightarrow 10$ |
| $T_{min} = 0.459$, $T_{max} = 0.754$ | $k = -25 \rightarrow 25$ |
| 39813 measured reflections | $l = -6 \rightarrow 7$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H atoms treated by a mixture of independent and constrained refinement |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.046$ | $w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 0.9951P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.106$ | |
| $S = 1.08$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 2060 reflections | $\Delta\rho_{max} = 0.18$ e Å$^{-3}$ |
| 173 parameters | $\Delta\rho_{min} = -0.22$ e Å$^{-3}$ |
| 172 restraints | Absolute structure: Refined as an inversion twin |
| Primary atom site location: shelXT | Absolute structure parameter: 0.3 (12) |
| Hydrogen site location: mixed | |

*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**. Refined as a 2-component inversion twin.

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

|       | $x$         | $y$          | $z$        | $U_{iso}$*/$U_{eq}$ |
| ----- | ----------- | ------------ | ---------- | ------------------- |
| N1    | 0.8644 (4)  | 0.33304 (16) | 0.4674 (6) | 0.0276 (8)          |
| H1A   | 0.855 (5)   | 0.325 (2)    | 0.332 (4)  | 0.058 (18)*         |
| H1B   | 0.950 (4)   | 0.321 (2)    | 0.516 (7)  | 0.052 (16)*         |
| N2    | 0.3459 (4)  | 0.76938 (14) | 0.2091 (6) | 0.0295 (9)          |
| H2A   | 0.293746    | 0.748604     | 0.114219   | 0.035*              |
| H2B   | 0.284518    | 0.793724     | 0.279538   | 0.035*              |
| C11   | 0.7832 (4)  | 0.43707 (17) | 0.3906 (6) | 0.0205 (9)          |
| H11   | 0.750058    | 0.424326     | 0.253757   | 0.025*              |
| C12   | 0.7645 (4)  | 0.49766 (16) | 0.4496 (6) | 0.0181 (8)          |
| C13   | 0.8118 (4)  | 0.51680 (17) | 0.6518 (6) | 0.0186 (8)          |
| C14   | 0.8763 (4)  | 0.47369 (16) | 0.7896 (7) | 0.0211 (8)          |
| H14   | 0.908901    | 0.485974     | 0.927203   | 0.025*              |
| C15   | 0.8932 (4)  | 0.41367 (17) | 0.7284 (7) | 0.0228 (9)          |
| H15   | 0.935284    | 0.385279     | 0.825644   | 0.027*              |
| C16   | 0.8497 (4)  | 0.39431 (17) | 0.5276 (7) | 0.0217 (9)          |
| C31   | 0.6953 (4)  | 0.54170 (17) | 0.2940 (6) | 0.0195 (8)          |
| H31A  | 0.692418    | 0.522457     | 0.151541   | 0.023*              |
| H31B  | 0.760925    | 0.577985     | 0.284019   | 0.023*              |
| C32   | 0.5330 (4)  | 0.56256 (16) | 0.3539 (6) | 0.0192 (8)          |
| H32A  | 0.467057    | 0.556422     | 0.228475   | 0.023*              |
| H32B  | 0.495208    | 0.535789     | 0.468896   | 0.023*              |
| C33   | 0.7993 (4)  | 0.58216 (16) | 0.7233 (7) | 0.0214 (8)          |
| H33A  | 0.836432    | 0.608605     | 0.606980   | 0.026*              |
| H33B  | 0.866689    | 0.588157     | 0.847236   | 0.026*              |
| C34   | 0.6377 (4)  | 0.60340 (17) | 0.7861 (6) | 0.0217 (8)          |
| H34A  | 0.572848    | 0.567063     | 0.802213   | 0.026*              |
| H34B  | 0.642990    | 0.623702     | 0.926614   | 0.026*              |
| C21   | 0.4468 (4)  | 0.66922 (16) | 0.2906 (7) | 0.0205 (8)          |
| H21   | 0.418445    | 0.656557     | 0.151499   | 0.025*              |
| C22   | 0.5171 (4)  | 0.62758 (17) | 0.4262 (6) | 0.0182 (8)          |
| C23   | 0.5629 (4)  | 0.64650 (17) | 0.6289 (6) | 0.0213 (8)          |
| C24   | 0.5334 (5)  | 0.70611 (17) | 0.6907 (7) | 0.0269 (9)          |
| H24   | 0.564002    | 0.719258     | 0.828207   | 0.032*              |
| C25   | 0.4600 (5)  | 0.74720 (19) | 0.5557 (7) | 0.0287 (10)         |
| H25   | 0.439745    | 0.787438     | 0.602401   | 0.034*              |
| C26   | 0.4170 (4)  | 0.72879 (17) | 0.3533 (7) | 0.0235 (9)          |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0259 (19) | 0.0224 (18) | 0.034 (2) | 0.0023 (15) | 0.0022 (17) | −0.0011 (16) |
| N2 | 0.0270 (18) | 0.0243 (18) | 0.037 (2) | 0.0035 (14) | −0.0119 (16) | 0.0037 (15) |
| C11 | 0.0109 (18) | 0.026 (2) | 0.025 (2) | −0.0010 (15) | −0.0004 (15) | 0.0018 (16) |
| C12 | 0.0108 (17) | 0.0217 (19) | 0.022 (2) | 0.0020 (15) | 0.0000 (16) | 0.0021 (16) |
| C13 | 0.0106 (17) | 0.0234 (18) | 0.022 (2) | 0.0013 (15) | 0.0018 (16) | −0.0004 (16) |
| C14 | 0.0129 (17) | 0.027 (2) | 0.023 (2) | −0.0011 (15) | 0.0004 (16) | 0.0019 (17) |
| C15 | 0.0153 (18) | 0.027 (2) | 0.026 (2) | 0.0022 (16) | 0.0008 (17) | 0.0042 (18) |
| C16 | 0.0179 (19) | 0.0185 (19) | 0.029 (2) | 0.0003 (15) | 0.0041 (17) | 0.0010 (17) |
| C31 | 0.0152 (18) | 0.0242 (19) | 0.019 (2) | 0.0001 (15) | −0.0003 (16) | −0.0019 (16) |
| C32 | 0.0140 (17) | 0.0197 (19) | 0.024 (2) | −0.0009 (14) | −0.0024 (16) | −0.0010 (15) |
| C33 | 0.0175 (18) | 0.0240 (19) | 0.023 (2) | −0.0017 (15) | 0.0000 (17) | −0.0019 (16) |
| C34 | 0.0232 (19) | 0.0210 (18) | 0.021 (2) | 0.0029 (16) | −0.0043 (17) | −0.0023 (16) |
| C21 | 0.0157 (18) | 0.0207 (18) | 0.025 (2) | −0.0007 (15) | −0.0031 (17) | 0.0004 (16) |
| C22 | 0.0141 (18) | 0.0189 (19) | 0.022 (2) | −0.0010 (14) | 0.0011 (16) | 0.0018 (15) |
| C23 | 0.0186 (19) | 0.0215 (19) | 0.024 (2) | 0.0000 (15) | −0.0030 (17) | −0.0006 (16) |
| C24 | 0.031 (2) | 0.023 (2) | 0.027 (2) | 0.0030 (18) | −0.0071 (17) | −0.0039 (18) |
| C25 | 0.032 (2) | 0.022 (2) | 0.032 (3) | 0.0022 (18) | −0.0055 (19) | −0.0045 (18) |
| C26 | 0.0185 (19) | 0.0217 (19) | 0.030 (2) | −0.0010 (16) | −0.0073 (17) | 0.0034 (17) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—H1A | 0.87 (2) | C31—C32 | 1.556 (5) |
| N1—H1B | 0.86 (2) | C32—H32A | 0.9900 |
| N1—C16 | 1.406 (5) | C32—H32B | 0.9900 |
| N2—H2A | 0.8817 | C32—C22 | 1.508 (5) |
| N2—H2B | 0.8824 | C33—H33A | 0.9900 |
| N2—C26 | 1.419 (5) | C33—H33B | 0.9900 |
| C11—H11 | 0.9500 | C33—C34 | 1.557 (5) |
| C11—C12 | 1.394 (5) | C34—H34A | 0.9900 |
| C11—C16 | 1.404 (5) | C34—H34B | 0.9900 |
| C12—C13 | 1.401 (5) | C34—C23 | 1.520 (5) |
| C12—C31 | 1.506 (5) | C21—H21 | 0.9500 |
| C13—C14 | 1.406 (5) | C21—C22 | 1.398 (5) |
| C13—C33 | 1.511 (5) | C21—C26 | 1.394 (5) |
| C14—H14 | 0.9500 | C22—C23 | 1.399 (6) |
| C14—C15 | 1.384 (5) | C23—C24 | 1.393 (5) |
| C15—H15 | 0.9500 | C24—H24 | 0.9500 |
| C15—C16 | 1.385 (6) | C24—C25 | 1.400 (6) |
| C31—H31A | 0.9900 | C25—H25 | 0.9500 |
| C31—H31B | 0.9900 | C25—C26 | 1.387 (6) |
| | | | |
| H1A—N1—H1B | 111 (4) | C22—C32—C31 | 116.1 (3) |
| C16—N1—H1A | 116 (3) | C22—C32—H32A | 108.3 |
| C16—N1—H1B | 107 (3) | C22—C32—H32B | 108.3 |
| H2A—N2—H2B | 109.3 | C13—C33—H33A | 108.4 |

| | | | |
|---|---|---|---|
| C26—N2—H2A | 109.7 | C13—C33—H33B | 108.4 |
| C26—N2—H2B | 109.6 | C13—C33—C34 | 115.4 (3) |
| C12—C11—H11 | 119.1 | H33A—C33—H33B | 107.5 |
| C12—C11—C16 | 121.9 (4) | C34—C33—H33A | 108.4 |
| C16—C11—H11 | 119.1 | C34—C33—H33B | 108.4 |
| C11—C12—C13 | 119.5 (4) | C33—C34—H34A | 108.5 |
| C11—C12—C31 | 119.5 (4) | C33—C34—H34B | 108.5 |
| C13—C12—C31 | 121.0 (3) | H34A—C34—H34B | 107.5 |
| C12—C13—C14 | 118.4 (4) | C23—C34—C33 | 115.1 (3) |
| C12—C13—C33 | 122.2 (3) | C23—C34—H34A | 108.5 |
| C14—C13—C33 | 119.3 (3) | C23—C34—H34B | 108.5 |
| C13—C14—H14 | 119.4 | C22—C21—H21 | 119.0 |
| C15—C14—C13 | 121.1 (4) | C26—C21—H21 | 119.0 |
| C15—C14—H14 | 119.4 | C26—C21—C22 | 121.9 (4) |
| C14—C15—H15 | 119.5 | C21—C22—C32 | 118.7 (3) |
| C14—C15—C16 | 121.1 (4) | C21—C22—C23 | 119.2 (3) |
| C16—C15—H15 | 119.5 | C23—C22—C32 | 121.9 (3) |
| C11—C16—N1 | 121.1 (4) | C22—C23—C34 | 122.1 (3) |
| C15—C16—N1 | 120.9 (4) | C24—C23—C34 | 119.3 (4) |
| C15—C16—C11 | 117.9 (3) | C24—C23—C22 | 118.6 (4) |
| C12—C31—H31A | 108.7 | C23—C24—H24 | 119.1 |
| C12—C31—H31B | 108.7 | C23—C24—C25 | 121.8 (4) |
| C12—C31—C32 | 114.2 (3) | C25—C24—H24 | 119.1 |
| H31A—C31—H31B | 107.6 | C24—C25—H25 | 120.2 |
| C32—C31—H31A | 108.7 | C26—C25—C24 | 119.6 (4) |
| C32—C31—H31B | 108.7 | C26—C25—H25 | 120.2 |
| C31—C32—H32A | 108.3 | C21—C26—N2 | 119.7 (4) |
| C31—C32—H32B | 108.3 | C25—C26—N2 | 121.5 (4) |
| H32A—C32—H32B | 107.4 | C25—C26—C21 | 118.8 (4) |
| | | | |
| C11—C12—C13—C14 | −0.3 (5) | C31—C32—C22—C21 | 108.3 (4) |
| C11—C12—C13—C33 | 178.1 (3) | C31—C32—C22—C23 | −75.3 (4) |
| C11—C12—C31—C32 | 108.7 (4) | C32—C22—C23—C34 | 2.6 (5) |
| C12—C11—C16—N1 | 178.4 (3) | C32—C22—C23—C24 | −174.8 (4) |
| C12—C11—C16—C15 | 1.8 (5) | C33—C13—C14—C15 | −178.4 (3) |
| C12—C13—C14—C15 | 0.0 (5) | C33—C34—C23—C22 | 68.8 (5) |
| C12—C13—C33—C34 | 76.1 (5) | C33—C34—C23—C24 | −113.8 (4) |
| C12—C31—C32—C22 | 109.5 (4) | C34—C23—C24—C25 | −177.7 (4) |
| C13—C12—C31—C32 | −71.9 (4) | C21—C22—C23—C34 | 179.0 (3) |
| C13—C14—C15—C16 | 1.3 (5) | C21—C22—C23—C24 | 1.6 (5) |
| C13—C33—C34—C23 | −107.9 (4) | C22—C21—C26—N2 | 179.7 (3) |
| C14—C13—C33—C34 | −105.6 (4) | C22—C21—C26—C25 | 0.7 (6) |
| C14—C15—C16—N1 | −178.8 (3) | C22—C23—C24—C25 | −0.2 (6) |
| C14—C15—C16—C11 | −2.1 (5) | C23—C24—C25—C26 | −1.0 (6) |
| C16—C11—C12—C13 | −0.6 (5) | C24—C25—C26—N2 | −178.3 (4) |
| C16—C11—C12—C31 | 178.8 (3) | C24—C25—C26—C21 | 0.7 (6) |
| C31—C12—C13—C14 | −179.7 (3) | C26—C21—C22—C32 | 174.7 (3) |
| C31—C12—C13—C33 | −1.3 (5) | C26—C21—C22—C23 | −1.9 (5) |

*Hydrogen-bond geometry (Å, º)*

*Cg*1 and *Cg*2 are the centroids of rings C11–C16 and C21–C26, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*B*···N2ⁱ | 0.86 (4) | 2.46 (4) | 3.295 (5) | 165 (4) |
| N2—H2*A*···N1ⁱⁱ | 0.88 | 2.46 | 3.295 (5) | 159 |
| N2—H2*B*···*Cg*2ⁱⁱⁱ | 0.88 | 2.96 | 3.742 (4) | 149 |
| C14—H14···*Cg*1ⁱᵛ | 0.95 | 2.84 | 3.572 (4) | 135 |
| C32—H32*A*···*Cg*1ⁱⁱ | 0.99 | 2.78 | 3.640 (4) | 145 |

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