Intermolecular hydrogen bonding in \(N\)-methyl-\(N'\)-(pyridin-2-yl)benzene-1,2-diamine

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The structure of \(N\)-methyl-\(N'\)-(pyridin-2-yl)benzene-1,2-diamine, \(C_{12}H_{13}N_3\), at 123 K has orthorhombic (\(Pna2_1\)) symmetry. The title compound displays an unexpected proton-splitting pattern when studied by \(^1\)H NMR spectroscopy. The X-ray crystallography analysis determined this to be caused by strong dual \(N\)–\(H\)···\(N\) hydrogen bonding.

1. Chemical context

\textit{ortho-}Phenylene diamine compounds are valuable precursors that have widespread use in a number of applications, especially as carbene ligands (Peris, 2018; Flanigan et al., 2015; Hopkinson et al., 2014; Fèvre et al., 2013; Velazquez & Verpoort, 2012; Doddi et al., 2019). The synthesis of \textit{ortho-}phenylene diamine derivatives, whether it be introducing functionality on the aryl ring or the nitrogen atom of the amine group, remains a challenge and continues to attract ongoing efforts to develop efficient synthetic routes to access a diverse library of functionalized compounds. We have been interested in functionalized symmetrical and unsymmetrical \textit{ortho-}phenylene diamine derivatives to access organometallic compounds for use in catalysis applications (Wang et al., 2013) and novel azaborole systems (Abbey & Liu, 2013; Weber, 2012, 2008; Segawa et al., 2009). Although a number of symmetrical ligands, such as I and II, are readily available commercially, unsymmetrical ligands, such III and IV, are less common because the chemical routes and purification processes to access these compounds are more complicated (substituted \textit{ortho-}phenylene diamine compounds I–VI of interest are shown in the scheme below).

![Image](https://example.com/image)

Compound IV was synthesized by a modification of a literature procedure (Wang et al., 2013). Analysis of the compound using \(^1\)H NMR spectroscopy to confirm the purity revealed some unexpected findings (see supporting information) when compared with similar compounds shown in the scheme. Upon initial purification and isolation of IV, analysis...
by proton NMR in CDCl₃ sometimes showed what seemed to be two different methyl signals, which we initially assumed was a contaminant originating from the reaction that could not be easily removed. However, analysis of the same material by ¹³C NMR spectroscopy showed a relatively simple and clean spectrum, suggesting signals for only a single compound or, if a second compound was present, the signals could be overlapping and therefore difficult to distinguish. Previously reported compounds I and II are both symmetrical and show very simple and expected signals in their respective ¹H NMR spectra (see Figs. S1 and S2). The methyl signal of I was found as a singlet at 2.9 ppm and NH protons as a broad singlet at 3.0–3.5 ppm. Meanwhile, compound II shows the NH protons occurring as a broad singlet further downfield at 5.5–5.7 ppm, presumably caused by deshielding effects of the aryl substituents. Analysis of compound IV in CDCl₃ shows well-defined signals that can be attributed to the aryl and pyridyl protons occurring in the downfield region between 6.3–8.3 ppm region (Fig. S3). The methyl signal occurs at 2.85 ppm, and it is interesting to see two different types of NH protons, a broad singlet at 4.1–4.5 ppm and a broad multiplet at 6.2–6.3 ppm. While we expect the chemical environments to be significantly different for the NH protons, we were unable to explain the multiplet-nature or coupling of these NH protons to another proton spin system. To further probe these unusual spectroscopic features, proton NMR analysis was undertaken in d₆-DMSO (Fig. S4), which resulted in significant sharpening of the NH signals. The initial broad NH peak now appears as a broad multiplet around 5 ppm, and the methyl signal is split into a second order doublet, which was very unexpected. 2D COSY spectroscopy in d₆-DMSO was performed on the same NMR sample (Fig. 1) and clearly showed the upfield NH multiplet at 5 ppm to be directly coupled through the nitrogen atom with the neighbouring protons on the methyl group. On the NMR time scale, proton-to-methyl coupling through the nitrogen atom is never reported as the NH proton is extremely labile (i.e. evident by very broad or even undetectable signals in proton NMR spectra) and readily undergoes facile exchange: to the best of our knowledge this type of NH proton coupling is exceptionally rare. In addition, the other downfield NH proton has sharpened further in d₆-DMSO and appears as a multiplet at 6.4–6.5 ppm, which suggests this NH proton may be involved in longer range coupling of the protons in the pyridyl ring. From the COSY spectrum, it appears that this NH proton is involved in long-range coupling with the pyridyl and/or phenyl protons. To understand the cause of this unexplained coupling observed in the ¹H NMR spectra for compound IV, analysis by X-ray crystallographic methods was undertaken.

2. Structural commentary

The molecular structure and atom-numbering scheme of the title compound is shown in Fig. 2. The asymmetric unit comprises two independent molecules assembled in a self-complementary N—H···N hydrogen-bonded dimer with a classical ring motif (Table 1). The overall configuration of the N’-(2-pyridyl)-benzene-1,2-diamine core of the molecule is very similar to that observed in the closely related compound, N’-(2-bromobenzyl)-N’-(2-pyridyl)-benzene-1,2-diamine.

![Figure 1](image1.png)

**Figure 1**
Two-dimensional COSY spectrum of N-methyl-N-phenyl-1,2-diamino-benzene, IV (d₆-DMSO).

![Figure 2](image2.png)

**Figure 2**
Molecular diagram of the title compound, with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size.

| D—H—A  | D—H | H—···A | D—···A | D—H—A |
|---------|------|--------|--------|--------|
| N4—H4—N2 | 0.90 (3) | 2.11 (3) | 3.001 (3) | 173 (2) |
| N1—H1—N5 | 0.88 (3) | 2.11 (3) | 2.981 (3) | 173 (2) |
| N6—H6—N2 | 0.88 (3) | 2.62 (2) | 3.374 (2) | 145 (2) |
| N3—H3—N5 | 0.87 (3) | 2.61 (3) | 3.337 (2) | 142 (2) |
Our current compound (Gdaniec et al., 2004) shows both conformations in a single molecule still forms the hydrogen-bonded dimer. The bulky 2-bromo-benzyl group attached to one amino group, it interacts with other functional groups (Takasuka et al., 1986). The structure of N-(2-pyridyl)-benzene-1,2-diamine, the second pyridyl ring is not co-planar, with an intermolecular C—H · · · N interaction between the pyridyl nitrogen atoms and the 2-aminobenzyl ring. The former leads to dimer formation such as observed for the parent compound 2-(phenylamino)pyridine (Polamo et al., 1997) and in the current example. In contrast, the latter conformation may lead to alternate structural motifs such as 1-D catemer chains (Talja & Polamo, 2005; Polamo & Talja, 2004) or interactions with other functional groups (Takasuka et al., 1986). The structure of N,N'-bis(2-pyridyl)benzene-1,2-diamine shows both conformations in a single molecule (Gdaniec et al., 2004).

Of greater interest is compound VI, which is very similar to our current compound IV. While compound VI contains the bulky 2-bromo-benzyl group attached to one amino group, it still forms the hydrogen-bonded dimer V complex. The reported proton NMR spectrum of V in CDCl3 (Manjare et al., 2009) reveals some interesting features that are similar to those of compound IV. The methylene protons on VI are magnetically non-equivalent whereby each proton has a different chemical shift of 4.83 and 4.41 ppm and are strongly coupled to each other. The two NH protons are also in different environments, one located downfield at 6.15 ppm as a multiplet and the other lies under a methylene proton signal at 4.41 ppm, which are essentially in the same location as for compound IV. Interestingly, as compound VI is only analysed in CDCl3, the authors do not observe any coupling of the NH proton with either of the methylene protons. We suspect the CH3—NH coupling observed in IV when using CDCl3 is less pronounced or enhanced by solvation effects than when using d6-DMSO. Nevertheless, the presence and observation of this CH3—NH coupling in compound IV, to the best of our knowledge, is rare, and in this case a result of the dual intermolecular hydrogen bonding, occurring from the primary amino-pyridine dimer complex and secondary pyridyl and CH3—NH interaction.

3. Supramolecular features

The crystal packing of the title compound involves no π–π ring interactions [minimum Cg...Cg separation 4.7654 (12) Å, dihedral angle 58.68 (10)°]. There are two minor C—H···Cg interactions linking the dimers into a supramolecular two-dimensional sheet lying parallel to the ab plane [Fig. 3; C12···Cg4' = 3.456 (3) Å, C12—H···Cg4' = 150°, H···Cg4' = 2.66 Å, and C24···Cg2ii = 3.565 (3) Å, C24—H···Cg2ii = 152°, H···Cg2ii = 2.67 Å; Cg2 and Cg4 are the centroids of rings C6—C11 and C18—C23, respectively; symmetry codes: (i) x − 1/2, y, z; (ii) 1/2 + x, 1/2 − y, z].

4. Database survey

A search of the Cambridge Structure Database (CSD version 5.43, November 2021; Groom et al., 2016) for substituted N-diamino-aryl molecules with at least one 2-pyridyl substituent on one of the nitrogen atoms results in only two other related compounds, N-(2-bromobenzyl)-N'-(2-pyridyl)-benzene-1,2-diamine (Manjare et al., 2009; CSD refcode RUFGIJ) and N,N'-bis(2-pyridyl)benzene-1,2-diamine (Gdaniec et al., 2004; CSD refcode ARUDEW). Both of these structures show the N—H···N hydrogen-bonded ring motif observed in the title compound. Interestingly, for N,N'-bis(2-pyridyl)benzene-1,2-diamine, the second pyridyl ring is not involved in N—H···N hydrogen bonding. Furthermore, the

Figure 3
A view of the unit-cell packing, showing a single 2-D layer of hydrogen-bonded dimer molecules.
related N,N’-bis(2-pyridyl)benzene-1,3-diamine and N,N’-bis(2-pyridyl)benzene-1,4-diamine compounds (Bensemann et al., 2002; CSD refcodes XILPEN, XILPUD01; Wichers & Gdaniec, 2011; CSD refcode XILPUD02) show a greater complexity of N—H⋯N hydrogen-bonding motifs.

5. Synthesis and crystallization

N,N’-Dimethyl-1,2-phenylenediamine I and N,N’-diphenyl-1,2-phenylenediamine II were obtained from commercial sources, while compound IV was synthesized following modification of a literature procedure (Wang et al., 2013). Interestingly, compounds I and II are liquids and dispose easily, possibly due to the presence of residual contaminants that may be difficult to remove completely during purification. This can make purification of the ligand difficult when the R groups are small (i.e. methyl). Introduction of bulky aryl groups provides materials that are crystalline and can be purified easily by chromatography and recrystallization. Compound IV was synthesized by methylation of commercially available N-(pyridin-2-yl)benzene-1,2-diamine by modifying literature conditions (Wang et al., 2013) to introduce the methyl group onto the primary amine functionality. This compound was purified by chromatographic methods to afford a white solid in high purity. A suitable sample for X-ray determination was achieved by the slow diffusion of petroleum ether into a solution of IV dissolved in ethyl acetate.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was solved in the non-centrosymmetric space group Pna21 and refined as a racemic twin [BASF 0.3 (5)]. Hydrogen atoms attached to carbon were placed in calculated positions and refined using a riding model. The hydrogen atoms of the NH groups were located in a difference-Fourier map, and freely refined.

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Computing details

Data collection: \textit{CrysAlis PRO} (Rigaku OD, 2015); cell refinement: \textit{CrysAlis PRO} (Rigaku OD, 2015); data reduction: \textit{CrysAlis PRO} (Rigaku OD, 2015); program(s) used to solve structure: \textit{SHELXT2018/3} (Sheldrick, 2015a); program(s) used to refine structure: \textit{SHELXL2018/3} (Sheldrick, 2015b); molecular graphics: \textit{X-SEED} (Barbour, 2001); software used to prepare material for publication: \textit{publCIF} (Westrip, 2010).

\textit{N}-methyl-\textit{N}'-(Pyridin-2-yl)benzene-1,2-diamine

\textbf{Crystal data}

\begin{itemize}
  \item \textit{C}_{12}\textit{H}_{13}\textit{N}_{3}
  \item \(M_r = 199.25\)
  \item Orthorhombic, \textit{P}na\textit{2}_1
  \item \(a = 13.4639\) (2) Å
  \item \(b = 7.8555\) (1) Å
  \item \(c = 20.1288\) (3) Å
  \item \(V = 2128.94\) (5) Å\(^3\)
  \item \(Z = 8\)
  \item \(F(000) = 848\)
\end{itemize}

\textbf{Data collection}

\begin{itemize}
  \item Oxford Diffraction Gemini Ultra CCD diffractometer
  \item Radiation source: fine focus sealed tube
  \item Detector resolution: 10.3389 pixels mm\(^{-1}\)
  \item \(\omega\) scans
  \item Absorption correction: multi-scan
  \item \(\omega\) scans
  \item \textit{(CrysAlisPro; Rigaku OD, 2015)}
  \item \(T_{\text{min}} = 0.989, T_{\text{max}} = 1.000\)
\end{itemize}

\textbf{Refinement}

\begin{itemize}
  \item Refinement on \(F^2\)
  \item Least-squares matrix: full
  \item \(R[F^2 > 2\sigma(F^2)] = 0.029\)
  \item \(wR(F^2) = 0.072\)
  \item \(S = 1.06\)
  \item 3104 reflections
  \item 290 parameters
  \item 1 restraint
  \item Hydrogen site location: mixed
  \item \(D_x = 1.243\) Mg m\(^{-3}\)
  \item Cu \(K\alpha\) radiation, \(\lambda = 1.54178\) Å
  \item Cell parameters from 6421 reflections
  \item \(\theta = 5.5\text{–}66.8^\circ\)
  \item \(\mu = 0.60\) mm\(^{-1}\)
  \item \(T = 123\) K
  \item Prism, colourless
  \item 0.25 \(\times\) 0.13 \(\times\) 0.10 mm
  \item 11852 measured reflections
  \item 3104 independent reflections
  \item 3018 reflections with \(I > 2\sigma(I)\)
  \item \(R_{\text{int}} = 0.022\)
  \item \(\theta_{\text{max}} = 66.8^\circ, \theta_{\text{min}} = 6.1^\circ\)
  \item \(h = -16\rightarrow15\)
  \item \(k = -9\rightarrow8\)
  \item \(l = -19\rightarrow23\)
\end{itemize}

H atoms treated by a mixture of independent and constrained refinement

\[w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.2845P]\]

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

\((\Delta/\sigma)_{\text{max}} < 0.001\)

\(\Delta\rho_{\text{max}} = 0.12\) e Å\(^{-3}\)

\(\Delta\rho_{\text{min}} = -0.16\) e Å\(^{-3}\)

Absolute structure: Refined as an inversion twin

Absolute structure parameter: 0.3 (5)
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    | Uiso*/*Ueq |
|----|------|------|------|------------|
| N1 | 0.05732 (12) | 0.4385 (2) | 0.17463 (9) | 0.0216 (4) |
| N2 | 0.17895 (11) | 0.6413 (2) | 0.18021 (8) | 0.0197 (3) |
| N3 | −0.12863 (12) | 0.4264 (2) | 0.23539 (10) | 0.0218 (4) |
| N4 | 0.20213 (12) | 0.5712 (2) | 0.32597 (9) | 0.0215 (4) |
| N5 | 0.08245 (12) | 0.3655 (2) | 0.31899 (9) | 0.0191 (3) |
| N6 | 0.38962 (12) | 0.5723 (2) | 0.26687 (9) | 0.0213 (4) |
| C1 | 0.10475 (13) | 0.5720 (2) | 0.14465 (10) | 0.0182 (4) |
| C2 | 0.07758 (14) | 0.6353 (3) | 0.08167 (10) | 0.0220 (4) |
| H2 | 0.024921 | 0.584736 | 0.057237 | 0.026* |
| C3 | 0.12892 (16) | 0.7717 (3) | 0.05649 (14) | 0.0276 (5) |
| H3A | 0.111761 | 0.816520 | 0.014189 | 0.033* |
| C4 | 0.20612 (16) | 0.8445 (3) | 0.09273 (12) | 0.0286 (5) |
| H4A | 0.242660 | 0.938570 | 0.075915 | 0.034* |
| C5 | 0.22743 (15) | 0.7749 (3) | 0.15392 (12) | 0.0229 (5) |
| H5 | 0.279645 | 0.824378 | 0.179112 | 0.027* |
| C6 | −0.01999 (14) | 0.3405 (2) | 0.14590 (10) | 0.0200 (4) |
| C7 | −0.00450 (17) | 0.2503 (3) | 0.08767 (13) | 0.0273 (5) |
| H7 | 0.058430 | 0.255938 | 0.066431 | 0.033* |
| C8 | −0.07908 (18) | 0.1521 (3) | 0.05989 (12) | 0.0325 (5) |
| H8 | −0.068144 | 0.092462 | 0.019500 | 0.039* |
| C9 | −0.17014 (17) | 0.1423 (3) | 0.09204 (12) | 0.0316 (5) |
| H9 | −0.221668 | 0.074427 | 0.073659 | 0.038* |
| C10 | −0.18668 (15) | 0.2303 (3) | 0.15057 (13) | 0.0244 (5) |
| H10 | −0.249258 | 0.221028 | 0.172068 | 0.029* |
| C11 | −0.11291 (14) | 0.3325 (2) | 0.17851 (10) | 0.0192 (4) |
| C12 | −0.21406 (16) | 0.3957 (3) | 0.27773 (12) | 0.0297 (5) |
| H12A | −0.274707 | 0.430287 | 0.254431 | 0.045* |
| H12B | −0.207321 | 0.461959 | 0.318748 | 0.045* |
| C13 | 0.15406 (13) | 0.4378 (2) | 0.35580 (10) | 0.0179 (4) |
| C14 | 0.17762 (14) | 0.3787 (3) | 0.41966 (11) | 0.0235 (4) |
| H14 | 0.228036 | 0.432290 | 0.445205 | 0.028* |
| C15 | 0.12622 (17) | 0.2417 (3) | 0.44443 (14) | 0.0281 (5) |
| H15 | 0.141481 | 0.198837 | 0.487358 | 0.034* |
| C16 | 0.05185 (16) | 0.1657 (3) | 0.40675 (12) | 0.0277 (5) |
| H16 | 0.015320 | 0.071136 | 0.423112 | 0.033* |
| C17 | 0.03327 (15) | 0.2328 (3) | 0.34494 (12) | 0.0230 (5) |
| H17 | −0.017626 | 0.181957 | 0.318960 | 0.028* |
| Atom | U\(^{11}\) (Å\(^2\)) | U\(^{12}\) (Å\(^2\)) | U\(^{13}\) (Å\(^2\)) | U\(^{22}\) (Å\(^2\)) | U\(^{23}\) (Å\(^2\)) | U\(^{33}\) (Å\(^2\)) |
|------|----------------|-----------------|-----------------|----------------|----------------|----------------|
| N1   | 0.0207 (8)    | 0.0279 (9)      | 0.0160 (9)      | -0.0072 (7)   | -0.0018 (7)   | 0.0013 (7)    |
| N2   | 0.0217 (7)    | 0.0207 (7)      | 0.0194 (8)      | -0.0011 (6)   | 0.0000 (6)    | -0.0029 (7)  |
| N3   | 0.0195 (8)    | 0.0224 (9)      | 0.0236 (9)      | -0.0020 (6)   | 0.0016 (7)    | -0.0022 (7)  |
| N4   | 0.0197 (8)    | 0.0283 (9)      | 0.0165 (9)      | -0.0069 (7)   | -0.0027 (7)   | 0.0031 (8)   |
| N5   | 0.0164 (7)    | 0.0216 (8)      | 0.0192 (8)      | -0.0005 (6)   | 0.0009 (6)    | -0.0004 (7)  |
| N6   | 0.0181 (8)    | 0.0228 (9)      | 0.0235 (9)      | -0.0027 (6)   | 0.0016 (7)    | -0.0012 (8)  |
| C1   | 0.0161 (8)    | 0.0197 (9)      | 0.0187 (10)     | 0.0009 (7)    | 0.0028 (7)    | -0.0035 (8)  |
| C2   | 0.0215 (9)    | 0.0246 (10)     | 0.0197 (10)     | 0.0011 (8)    | -0.0004 (8)   | -0.0016 (9)  |
| C3   | 0.0329 (12)   | 0.0271 (11)     | 0.0226 (12)     | 0.0000 (9)    | -0.0001 (9)   | 0.0048 (10)  |
| C4   | 0.0341 (11)   | 0.0241 (10)     | 0.0278 (12)     | -0.0064 (9)   | 0.0034 (9)    | 0.0025 (9)   |
| C5   | 0.0223 (9)    | 0.0237 (9)      | 0.0227 (13)     | -0.0056 (8)   | 0.0021 (8)    | -0.0027 (9)  |
| C6   | 0.0204 (9)    | 0.0208 (9)      | 0.0187 (10)     | -0.0035 (7)   | -0.0011 (8)   | 0.0030 (8)   |
| C7   | 0.0295 (11)   | 0.0301 (12)     | 0.0222 (13)     | -0.0054 (9)   | 0.0028 (9)    | -0.0011 (9)  |
| C8   | 0.0454 (13)   | 0.0309 (12)     | 0.0212 (11)     | -0.0094 (10)  | -0.0003 (10)  | -0.0052 (10) |
| C9   | 0.0385 (12)   | 0.0300 (11)     | 0.0263 (12)     | -0.0141 (9)   | -0.0099 (10)  | 0.0005 (10)  |
| C10  | 0.0216 (9)    | 0.0251 (10)     | 0.0265 (13)     | -0.0049 (8)   | -0.0026 (9)   | 0.0056 (9)   |
| C11  | 0.0207 (9)    | 0.0169 (9)      | 0.0200 (10)     | 0.0004 (7)    | -0.0033 (8)   | 0.0038 (8)   |
| C12  | 0.0263 (11)   | 0.0295 (11)     | 0.0333 (13)     | -0.0034 (9)   | 0.0102 (9)    | -0.0011 (10) |
| C13  | 0.0149 (8)    | 0.0203 (9)      | 0.0185 (10)     | 0.0010 (7)    | 0.0029 (7)    | -0.0024 (8)  |
| C14  | 0.0215 (9)    | 0.0266 (10)     | 0.0224 (12)     | -0.0012 (8)   | -0.0046 (8)   | 0.0004 (9)   |
| C15  | 0.0349 (13)   | 0.0280 (11)     | 0.0213 (12)     | -0.0011 (9)   | -0.0042 (9)   | 0.0061 (9)   |
| C16  | 0.0306 (10)   | 0.0227 (10)     | 0.0299 (12)     | -0.0056 (8)   | 0.0000 (9)    | 0.0044 (9)   |
| C17  | 0.0217 (10)   | 0.0204 (9)      | 0.0270 (14)     | -0.0024 (8)   | -0.0013 (8)   | -0.0033 (9)  |
| C18  | 0.0187 (9)    | 0.0220 (9)      | 0.0181 (10)     | -0.0036 (7)   | -0.0030 (8)   | 0.0031 (8)   |
| C19  | 0.0255 (10)   | 0.0289 (12)     | 0.0213 (13)     | -0.0036 (8)   | 0.0035 (9)    | 0.0002 (9)   |
| C20  | 0.0373 (12)   | 0.0349 (11)     | 0.0198 (11)     | -0.0098 (10)  | 0.0007 (9)    | -0.0060 (10) |

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### Geometric parameters (Å, ‰)

|   | C1   | N1   | N2   | N3   | N4   | N5   | N6   | C7   | C8   | C9   | C10  | C11  | C12  | C13  | C14  | C15  | C16  | C17  | C18  | C19  | C20  | C21  | C22  | C23  | C24  |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|   | 1.368 (3) | 1.418 (3) | 1.344 (3) | 1.344 (2) | 1.378 (3) | 1.452 (3) | 1.370 (3) | 1.418 (3) | 1.341 (3) | 1.342 (3) | 1.384 (3) | 1.451 (3) | 1.410 (3) | 1.372 (3) | 1.393 (3) | 1.378 (3) | 1.368 (3) | 1.418 (3) | 1.344 (3) | 1.344 (2) | 1.378 (3) | 1.452 (3) | 1.370 (3) | 1.418 (3) | 1.341 (3) | 1.342 (3) | 1.384 (3) | 1.451 (3) | 1.410 (3) | 1.372 (3) | 1.393 (3) | 1.378 (3) |
|   | C6   | C7   | C8   | C9   | C10  | C11  | C12  | C13  | C14  | C15  | C16  | C17  | C18  | C19  | C20  | C21  | C22  | C23  | C24  | C1   | N1   | N2   | N3   | N4   | N5   | N6   | N7   | N8   | N9   | N10  |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|   | C1   | N1   | N2   | N3   | N4   | N5   | N6   | C7   | C8   | C9   | C10  | C11  | C12  | C13  | C14  | C15  | C16  | C17  | C18  | C19  | C20  | C21  | C22  | C23  | C24  | C1   | N1   | N2   | N3   | N4   | N5   | N6   | N7   | N8   | N9   | N10  |
|   | 125.37 (18) | 117.88 (18) | 121.38 (17) | 124.93 (17) | 117.96 (18) | 120.93 (17) | 115.00 (17) | 121.89 (18) | 123.09 (18) | 118.5 (2) | 120.2 (2) | 117.4 (2) | 124.1 (2) | 120.20 (18) | 120.80 (18) | 118.97 (17) | 121.2 (2) | 118.9 (2) | 120.7 (2) | 121.1 (2) | 118.97 (17) | 120.20 (18) | 120.80 (18) | 118.97 (17) | 121.2 (2) | 118.9 (2) | 120.7 (2) | 121.1 (2) | 118.97 (17) | 120.20 (18) | 120.80 (18) | 118.97 (17) | 121.2 (2) | 118.9 (2) | 120.7 (2) | 121.1 (2) |
|   | N3   | C11  | C12  | C13  | C14  | C15  | C16  | C17  | C18  | C19  | C20  | C21  | C22  | C23  | C24  | C1   | N1   | N2   | N3   | N4   | N5   | N6   | N7   | N8   | N9   | N10  |
|   | 122.23 (18) | 119.83 (17) | 117.92 (19) | 114.92 (17) | 121.87 (18) | 123.21 (18) | 118.6 (2) | 120.1 (2) | 117.4 (2) | 124.1 (2) | 120.39 (18) | 120.74 (18) | 118.84 (17) | 120.9 (2) | 119.2 (2) | 120.64 (19) | 120.9 (2) | 121.96 (19) | 120.07 (17) | 117.95 (19) |
Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H  | H···A  | D···A  | D—H···A |
|----------|------|-------|--------|---------|
| N4—H4···N2 | 0.90 (3) | 2.11 (3) | 3.001 (3) | 173 (2) |
| N1—H1···N5 | 0.88 (3) | 2.11 (3) | 2.981 (3) | 173 (2) |
| N6—H6···N2 | 0.88 (3) | 2.62 (2) | 3.374 (2) | 145 (2) |
| N3—H3···N5 | 0.87 (3) | 2.61 (3) | 3.337 (2) | 142 (2) |