Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure and Hirshfeld surface analysis of 5,7-diphenyl-1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]-pyridine-6,6,8-tricarbonitrile methanol monosolvate

Farid N. Naghiyev,[a] Gunay Z. Mammadova,[a] Ali N. Khalilov,[a,b] Zeliha Atioğlu,[c] Mehmet Akkurt,[d] Anzurat A. Akobirshoeva[e]* and İbrahim G. Mamedov[a]

[a]Department of Chemistry, Baku State University, Z. Khalilov str. 23, Az, 1148 Baku, Azerbaijan, [b]"Composite Materials" Scientific Research Center, Azerbaijan State Economic University (UNEC), H. Aliyev str. 135, Az 1063, Baku, Azerbaijan, [c]Department of Aircraft Electrics and Electronics, School of Applied Sciences, Cappadocia University, Mustafapaşa, 50420 Ürgüp, Nevşehir, Turkey, [d]Department of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey, and [e]Acad. Sci. Republ. Tadzhikistan, Kh. Yu. Yusufbekov Pamir Biol. Inst., 1 Kholdorova St, Khorog 736002, Gbao, Tajikistan. *Correspondence e-mail: anzurat2003@mail.ru

Received 21 April 2021
Accepted 2 May 2021

Edited by L. Van Meervelt, Katholieke Universiteit Leuven, Belgium

Keywords: crystal structure; imidazolidine ring; pyridine ring; hydrogen bond; Hirshfeld surface analysis.

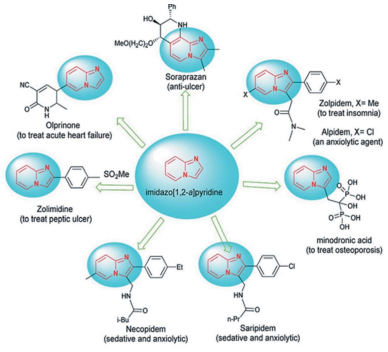
CCDC reference: 2081515

Supporting information: this article has supporting information at journals.iucr.org/e

In the title compound, $C_{22}H_{17}N_5\cdot CH_4O$, the imidazolidine ring of the 1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]pyridine ring system is a twisted envelope, while the 1,2,3,4-tetrahydropyridine ring adopts a twisted boat conformation. In the crystal, pairs of molecules are linked by O—H···N and N—H···O hydrogen bonds *via* two methanol molecules, forming a centrosymmetric $R_4^4(16)$ ring motif. These motifs are connected to each other by C—H···N hydrogen bonds and form columns along the *a* axis. The columns form a stable molecular packing, being connected to each other by van der Waals interactions. A Hirshfeld surface analysis indicates that the most significant contributions to the crystal packing are from H···H (43.8%), N···H/H···N (31.7%) and C···H/H···C (18.4%) contacts.

1. Chemical context

Having a great methodological diversity, C—C and C—*X* (where *X* is a heteroatom) bond-forming reactions lie at the heart of synthetic organic chemistry (Khalilov *et al.*, 2018*a*,*b*; Maharramov *et al.*, 2019; Cheng & Mankad, 2020). They allow the construction of complex molecular structures and the introduction of various substituents. Nowadays, researchers are constantly trying to develop new methods in these directions for the syntheses of structurally diverse valuable molecular entities. These approaches have successfully found application in the building of carbo- and heterocyclic ring systems (Naghiyev *et al.*, 2020; Mamedov *et al.*, 2019). In heterocyclic ring systems, the use of nitrogen as a bridgehead atom is being assessed widely. Bridgehead nitrogen heterocycles incorporating an imidazole ring are widespread structural motifs in a diverse range of compounds having application in medicinal chemistry, coordination chemistry, catalysis and materials science (Asadov *et al.*, 2016; Ma *et al.*, 2017*a*,*b*, 2020, 2021; Maharramov *et al.*, 2010, 2018; Mahmoudi *et al.*, 2017, 2019; Mahmudov *et al.*, 2019, 2020). Various synthetic drugs, such as soraprazan, alpidem, olprinone, saripidem, necopidem, minodronic acid, zolimidine and zolpidem containing the imidazo[1,2-*a*]pyridine moiety (Fig. 1) have already been used in medical practice (Hosseini & Bayat, 2018).



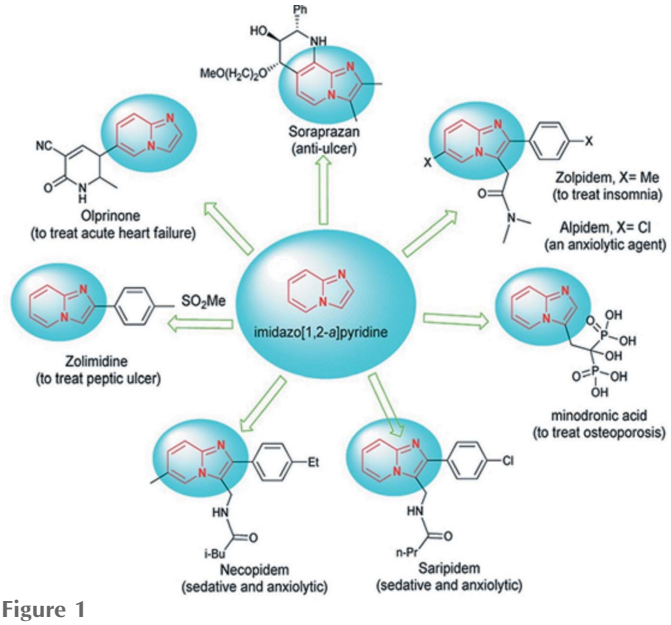
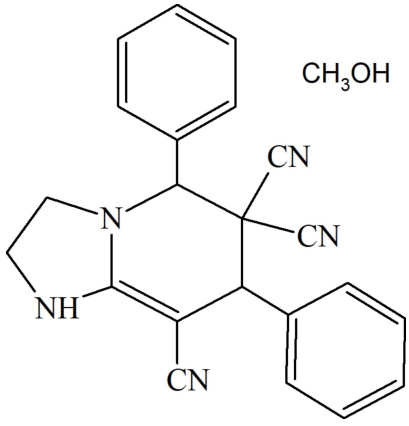


Figure 1
Drugs containing the imidazo[1,2-*a*]pyridine motif.

In the framework of our ongoing structural studies (Naghiyev *et al.*, 2021), herein we report the crystal structure and Hirshfeld surface analysis of the title compound, 5,7-diphenyl-1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]pyridine-6,6,8-tricarbonitrile methanol monosolvate.



2. Structural commentary

In the title compound, (Fig. 2), the imidazolidine ring (N1/N2/C1–C3) of the 1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]pyridine ring system (N1/N2/C1–C7) is a twisted envelope [with puckering parameters (Cremer & Pople, 1975) $Q(2)$ = 0.2844 (16) Å and $\varphi(2)$ = 226.3 (3)°], while the 1,2,3,4-tetrahydropyridine ring (N1/C3–C7) adopts a twisted boat conformation with Q_T = 0.5368 (14) Å, θ = 135.38 (15)°, φ = 82.6 (2)°. The C9–C14 and C17–C22 phenyl rings, which are attached to C5 and C7, respectively, are in equatorial positions (Fig. 2) and make dihedral angles of 64.00 (7) and 65.90 (7)°, respectively, with the mean plane of the 1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]pyridine ring system. The dihedral angle between the phenyl rings is 61.43 (8)°. The molecular conformation of the title compound is stabilized by an N2—H2*N*···O1 hydrogen bond (Fig. 2, Table 1).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H*O*1···N3^{i}	0.92 (3)	2.02 (3)	2.907 (2)	161 (2)
N2—H2*N*···O1	0.887 (18)	2.004 (18)	2.870 (2)	165.0 (16)
C7—H7···N3^{ii}	0.98	2.52	3.3742 (19)	146

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, pairs of molecules are linked by O—H···N, C—H···N and N—H···O hydrogen bonds *via* two methanol molecules, forming a centrosymmetric $R_4^4(16)$ ring motif (Bernstein *et al.*, 1995; Table 1; Fig. 3). These motifs are connected to each other by C—H···N hydrogen bonds and form columns along the *a*-axis direction (Figs. 4 and 5). The columns form a stable molecular packing, being connected to each other by van der Waals interactions.

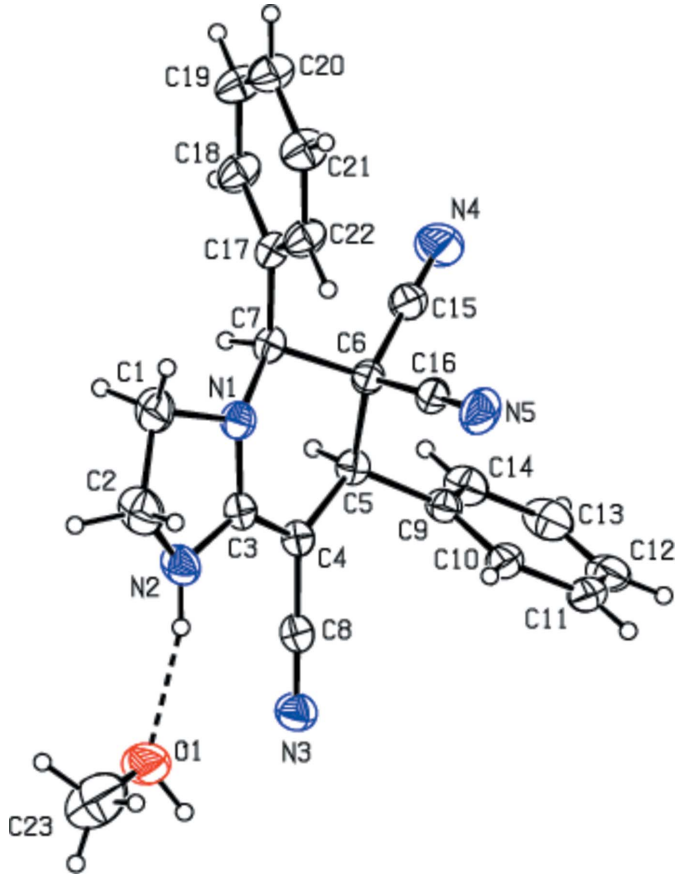


Figure 2
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. The dashed line indicates a N—H···O hydrogen bond.

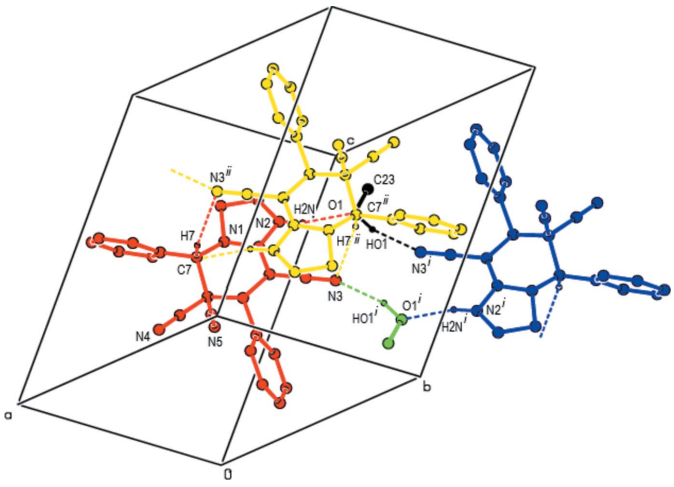


Figure 3
Details of the O—H···N, C—H···N and N—H···O hydrogen bonds (dashed lines) in the unit cell of the title compound. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$.]

To further investigate and visualize the intermolecular interactions of the title compound, the *CrystalExplorer* program (Turner *et al.*, 2017) was used. The interactions between the corresponding donor and acceptor atoms are visualized as bright-red spots on the Hirshfeld surface mapped over $d_{\rm norm}$ (Fig. 6), corresponding to O1—H*O*1···N3, C7—H7···N3 and N2—H2*N*···O1 hydrogen bonds. The other red spots correspond to weaker van der Waals interactions, of which the details are listed in Table 2.

The overall two-dimensional fingerprint plot of the title structure and H···H, N···H/H···N and C···H/H···C contacts are illustrated in Fig. 7*a*–*d*). The greatest contribution to the overall Hirshfeld surface results from H···H contacts with a

Table 2
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
H2*N*···O1	2.00	x, y, z
H7···N3	2.52	$1-x, 1-y, 1-z$
N3···H18	2.75	$-1+x, y, z$
N3···H*O*1	2.02	$-x, 1-y, 1-z$
N5···H1*B*	2.75	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
N5···H23*B*	2.77	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
H12···H12	2.54	$-x, 1-y, -z$
C20···H2*B*	3.02	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
H5···O1	2.79	$1-x, 1-y, 1-z$
H12···C23	3.07	$x, y, -1+z$

43.8% contribution (Fig. 7*b*). The relative contributions of the other interactions in descending order are: N···H/H···N (31.7%), C···H/H···C (18.4%), O···H/H···O (2.6%), C···C (2.4%), N···O/O···N (0.1%) and C···O/O···C (0.1%). The large contributions of H···H, N···H/H···N and C···H/H···C interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing (Hathwar *et al.*, 2015).

4. Database survey

A survey of the Cambridge Structural Database (CSD version 5.41, update of March 2020; Groom *et al.*, 2016) reveals two related compounds having the 1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]pyridine ring system of the title compound: ethyl 8-benzoyl-5-oxo-7-phenyl-1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]pyridine-6-carboxylate (refcode ADETUZ; Yu *et al.*, 2006) and 1-[(6-chloropyridin-3-yl)methyl]-5-ethoxy-8-nitro-1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]pyridine (BUDZAC; Tian *et al.*, 2009).

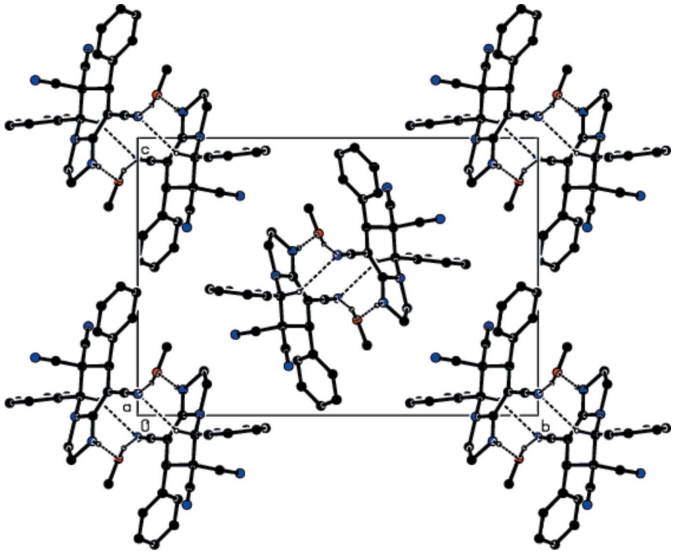


Figure 4
A view along the *a* axis of the columns that are formed by the O—H···N, C—H···N and N—H···O hydrogen bonds (dashed lines) in the title compound. H atoms not involved in hydrogen bonding have been omitted for clarity.

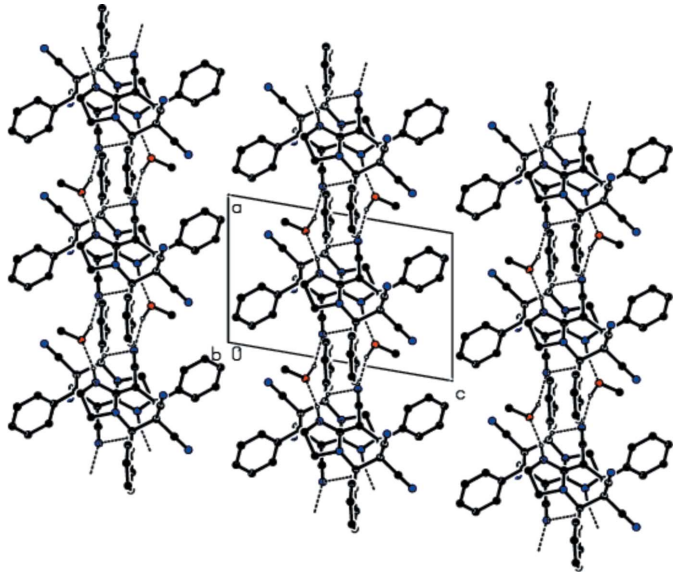


Figure 5
A part of view along the *b* axis of the columns shown in Fig. 4. H atoms not involved in hydrogen bonding have been omitted for clarity. Dashed lines indicate hydrogen bonds.

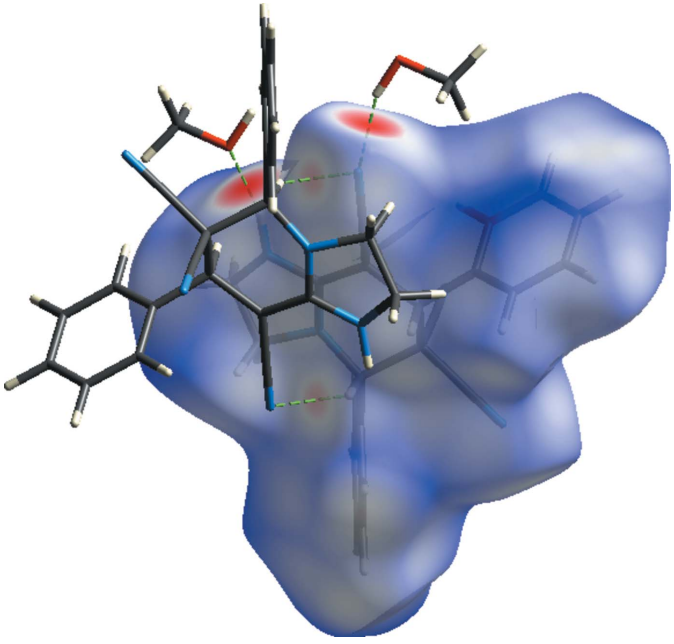


Figure 6
The three-dimensional Hirshfeld surface of the title compound plotted over d_{norm} in the range −0.5585 to +1.5646 a.u. The O—H···N, C—H···O and N—H···O hydrogen bonds are shown as dashed lines.

In ADETUZ, the six-membered ring adopts a twist-boat conformation. The molecules form dimeric associations *via* inversion-generated pairs of N—H···O hydrogen bonds. In BUDZAC, the fused pyridine ring adopts a twisted sofa conformation. The molecular structure features close intramolecular C—H···N and C—H···O hydrogen bonding.

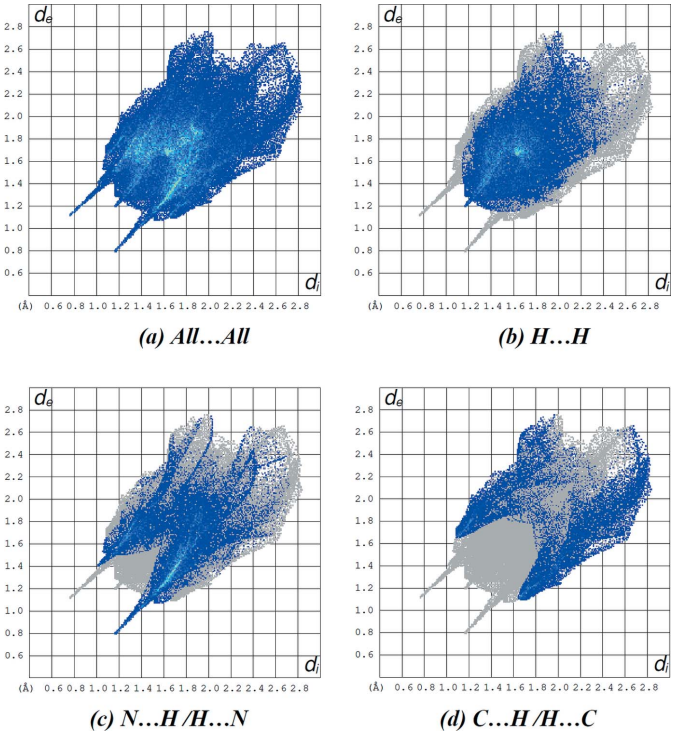


Figure 7
The two-dimensional fingerprint plots of the title compound, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) N···H/H···N, and (*d*) C···H/H···C interactions [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{17}N_5{\cdot}CH_4O$
M_r	383.45
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	8.5517 (10), 18.781 (2), 13.1925 (14)
β (°)	99.757 (4)
V (Å^3)	2088.2 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.28 × 0.26 × 0.25
Data collection	
Diffractometer	Bruker APEXII CCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33652, 4239, 3656
R_{int}	0.033
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.123, 1.03
No. of reflections	4239
No. of parameters	269
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.23

Computer programs: *APEX2* (Bruker, 2018), *SAINT* (Bruker, 2013), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

5. Synthesis and crystallization

To a solution of benzylidenemalononitrile (0.78 g; 5.1 mmol) in ethanol (30 mL), ethylenediamine (0.31 g; 5.2 mmol) was added and the mixture was refluxed for 7 h. Then 25 mL of ethanol were removed from the reaction mixture, which was left overnight. The precipitated crystals were separated by filtration and recrystallized from methanol (yield 47%; m.p. 443–444 K).

^{1}H NMR (300 MHz, DMSO-d_6): 3.18 (*t*, 2H, NCH_2); 3.42 (*t*, 2H, NCH_2); 4.79 (*s*, 1H, CH-Ar); 5.19 (*s*, 1H, CH-Ar); 7.41–7.58 (*m*, 10H, 10Ar-H); 7.70 (*s*, 1H, NH).^{13}C NMR (75 MHz, DMSO-d_6): 42.04 (NCH_2), 47.67 (CH-Ar), 48.41 (C_{quart}), 48.64 (=C_{quart}), 49.05 (NCH_2), 63.46 (CH-Ar), 112.91 (CN), 113.69 (CN), 121.24 (CN), 129.03 (4CH_{arom}), 129.42 (2CH_{arom}), 129.72 (CH_{arom}), 129.96 (2CH_{arom}), 130.85 (CH_{arom}), 133.25 (C_{arom}),135.90 ($C_{ar.}$), 162.08 (=C_{quart}).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C-bound H atoms were placed

in calculated positions (C—H = 0.93–0.98 Å) and refined as riding with U_{iso}(H) = 1.2 or 1.5U_{eq}(C). The H atoms of the amine and hydroxyl groups were located in a difference map [N2—H2*N* = 0.887 (18) Å and O1—H*O*1 = 0.92 (3) Å] and were refined with the constraint U_{iso}(H) = 1.2U_{eq}(N) or 1.5U_{eq}(O).

Acknowledgements

Author contributions are as follows. Conceptualization, FNN and IGM; methodology, GZM, MA and FNN; investigation, ZA, AAA and FNN; writing (original draft), MA and ANK; writing (review and editing of the manuscript), MA, IGM and ANK; visualization, MA and ANK; funding acquisition, IGM, and FNN; resources, GZM, AAA, MA and FNN; supervision, MA, IGM and ANK.

Funding information

This work was supported by Baku State University and UNEC Research Program.

References

Asadov, Z. H., Rahimov, R. A., Ahmadova, G. A., Mammadova, K. A. & Gurbanov, A. V. (2016). *J. Surfactants Deterg*. **19**, 145–153.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (2013). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2018). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cheng, L.-J. & Mankad, N. P. (2020). *Chem. Soc. Rev*. **49**, 8036–8064.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Hathwar, V. R., Sist, M., Jørgensen, M. R. V., Mamakhel, A. H., Wang, X., Hoffmann, C. M., Sugimoto, K., Overgaard, J. & Iversen, B. B. (2015). *IUCrJ*, **2**, 563–574.

Hosseini, H. & Bayat, M. (2018). *RSC Adv*. **8**, 41218–41225.

Khalilov, A. N., Asgarova, A. R., Gurbanov, A. V., Maharramov, A. M., Nagiyev, F. N. & Brito, I. (2018*a*). *Z. Kristallogr. NCS* **233**, 1019–1020.

Khalilov, A. N., Asgarova, A. R., Gurbanov, A. V., Nagiyev, F. N. & Brito, I. (2018*b*). *Z. Kristallogr. New Cryst. Struct.* **233**, 947–948.

Ma, Z., Gurbanov, A. V., Maharramov, A. M., Guseinov, F. I., Kopylovich, M. N., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2017*a*). *J. Mol. Catal. A Chem.* **426**, 526–533.

Ma, Z., Gurbanov, A. V., Sutradhar, M., Kopylovich, M. N., Mahmudov, K. T., Maharramov, A. M., Guseinov, F. I., Zubkov, F. I. & Pombeiro, A. J. L. (2017*b*). *Mol. Catal.* **428**, 17–23.

Ma, Z., Mahmudov, K. T., Aliyeva, V. A., Gurbanov, A. V., Guedes da Silva, M. F. C. & Pombeiro, A. J. L. (2021). *Coord. Chem. Rev*. **437**, 213859.

Ma, Z., Mahmudov, K. T., Aliyeva, V. A., Gurbanov, A. V. & Pombeiro, A. J. L. (2020). *Coord. Chem. Rev*. **423**, 213482.

Maharramov, A. M., Aliyeva, R. A., Aliyev, I. A., Pashaev, F. G., Gasanov, A. G., Azimova, S. I., Askerov, R. K., Kurbanov, A. V. & Mahmudov, K. T. (2010). *Dyes Pigments*, **85**, 1–6.

Maharramov, A. M., Duruskari, G. S., Mammadova, G. Z., Khalilov, A. N., Aslanova, J. M., Cisterna, J., Cárdenas, A. & Brito, I. (2019). *J. Chil. Chem. Soc.* **64**, 4441–4447.

Maharramov, A. M., Shikhaliyev, N. Q., Suleymanova, G. T., Gurbanov, A. V., Babayeva, G. V., Mammadova, G. Z., Zubkov, F. I., Nenajdenko, V. G., Mahmudov, K. T. & Pombeiro, A. J. L. (2018). *Dyes Pigments*, **159**, 135–141.

Mahmoudi, G., Dey, L., Chowdhury, H., Bauzá, A., Ghosh, B. K., Kirillov, A. M., Seth, S. K., Gurbanov, A. V. & Frontera, A. (2017). *Inorg. Chim. Acta*, **461**, 192–205.

Mahmoudi, G., Khandar, A. A., Afkhami, F. A., Miroslaw, B., Gurbanov, A. V., Zubkov, F. I., Kennedy, A., Franconetti, A. & Frontera, A. (2019). *CrystEngComm*, **21**, 108–117.

Mahmudov, K. T., Gurbanov, A. V., Aliyeva, V. A., Resnati, G. & Pombeiro, A. J. L. (2020). *Coord. Chem. Rev*. **418**, 213381.

Mahmudov, K. T., Gurbanov, A. V., Guseinov, F. I. & Guedes da Silva, M. F. C. (2019). *Coord. Chem. Rev*. **387**, 32–46.

Mamedov, I. G., Khrustalev, V. N., Dorovatovskii, P. V., Naghiev, F. N. & Maharramov, A. M. (2019). *Mendeleev Commun.* **29**, 232–233.

Naghiyev, F. N., Cisterna, J., Khalilov, A. N., Maharramov, A. M., Askerov, R. K., Asadov, K. A., Mamedov, I. G., Salmanli, K. S., Cárdenas, A. & Brito, I. (2020). *Molecules*, **25**, 2235–2248.

Naghiyev, F. N., Grishina, M. M., Khrustalev, V. N., Khalilov, A. N., Akkurt, M., Akobirshoeva, A. A. & Mamedov, İ. G. (2021). *Acta Cryst.* E**77**, 195–199.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.

Tian, Z., Li, D. & Li, Z. (2009). *Acta Cryst.* E**65**, o2517.

Turner, M. J., Mckinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer*17. University of Western Australia.

Yu, C.-Y., Yan, S.-J. & Huang, Z.-T. (2006). *Acta Cryst.* E**62**, o2731–o2733.

supporting information

Acta Cryst. (2021). E**77**, 600-604 [https://doi.org/10.1107/S2056989021004655]

Crystal structure and Hirshfeld surface analysis of 5,7-diphenyl-1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]pyridine-6,6,8-tricarbonitrile methanol monosolvate

Farid N. Naghiyev, Gunay Z. Mammadova, Ali N. Khalilov, Zeliha Atioğlu, Mehmet Akkurt, Anzurat A. Akobirshoeva and İbrahim G. Mamedov

Computing details

Data collection: *APEX2* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

5,7-Diphenyl-1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]pyridine-6,6,8-tricarbonitrile methanol monosolvate

Crystal data

$C_{22}H_{17}N_5 \cdot CH_4O$
$M_r = 383.45$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 8.5517$ (10) Å
$b = 18.781$ (2) Å
$c = 13.1925$ (14) Å
$\beta = 99.757$ (4)°
$V = 2088.2$ (4) Å^3
$Z = 4$
$F(000) = 808$
$D_x = 1.220$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9885 reflections
$\theta = 3.1$–26.4°
$\mu = 0.08$ mm^{-1}
$T = 296$ K
Block, colourless
0.28 × 0.26 × 0.25 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
33652 measured reflections
4239 independent reflections
3656 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 26.4°$, $\theta_{min} = 2.7°$
$h = -10 \rightarrow 10$
$k = -23 \rightarrow 23$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.123$
$S = 1.02$
4239 reflections
269 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.5899P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating -R-factor-obs 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.60712 (14)	0.34477 (6)	0.50461 (8)	0.0455 (3)
N2	0.42807 (17)	0.38674 (7)	0.59278 (9)	0.0554 (4)
N3	0.16518 (16)	0.50048 (7)	0.42172 (10)	0.0564 (4)
N4	0.77545 (19)	0.37704 (11)	0.17841 (12)	0.0818 (7)
N5	0.43619 (17)	0.24442 (8)	0.29156 (13)	0.0687 (5)
C1	0.6680 (2)	0.32722 (10)	0.61313 (11)	0.0610 (5)
O1	0.15621 (16)	0.45171 (9)	0.65565 (10)	0.0796 (5)
C2	0.5187 (2)	0.33436 (11)	0.66018 (13)	0.0728 (6)
C3	0.47744 (16)	0.38817 (7)	0.50125 (10)	0.0416 (4)
C4	0.41241 (15)	0.42550 (7)	0.41462 (9)	0.0400 (4)
C5	0.49374 (15)	0.42867 (7)	0.32123 (9)	0.0400 (3)
C6	0.60291 (14)	0.36144 (7)	0.32248 (9)	0.0396 (4)
C7	0.71275 (15)	0.35675 (7)	0.43062 (10)	0.0406 (3)
C8	0.27705 (16)	0.46706 (7)	0.41791 (10)	0.0430 (4)
C9	0.38002 (16)	0.43787 (7)	0.22050 (10)	0.0435 (4)
C10	0.24007 (17)	0.39947 (9)	0.19806 (11)	0.0529 (5)
C11	0.14001 (19)	0.40923 (12)	0.10485 (13)	0.0698 (6)
C12	0.1790 (2)	0.45789 (13)	0.03484 (12)	0.0768 (7)
C13	0.3160 (3)	0.49685 (11)	0.05680 (13)	0.0726 (7)
C14	0.4164 (2)	0.48700 (9)	0.14907 (12)	0.0567 (5)
C15	0.70149 (17)	0.36934 (9)	0.24146 (11)	0.0519 (4)
C16	0.50897 (16)	0.29533 (7)	0.30346 (11)	0.0456 (4)
C17	0.84126 (15)	0.30107 (7)	0.43683 (10)	0.0422 (4)
C18	0.99408 (17)	0.32313 (8)	0.43065 (13)	0.0555 (5)
C19	1.11587 (18)	0.27445 (10)	0.43609 (15)	0.0650 (6)
C20	1.08799 (19)	0.20309 (9)	0.44872 (14)	0.0622 (6)
C21	0.93680 (19)	0.18065 (8)	0.45511 (14)	0.0615 (5)
C22	0.81374 (17)	0.22886 (8)	0.44866 (12)	0.0519 (4)
C23	0.1184 (3)	0.4273 (2)	0.74675 (18)	0.1210 (12)
H1A	0.74920	0.36056	0.64351	0.0730*
H1B	0.71018	0.27920	0.62033	0.0730*
H2A	0.46245	0.28943	0.65878	0.0870*
H2B	0.54270	0.35144	0.73049	0.0870*
H2N	0.334 (2)	0.4024 (10)	0.6028 (14)	0.0660*
H5	0.56337	0.47045	0.32956	0.0480*

H7	0.76386	0.40317	0.44550	0.0490*
H10	0.21323	0.36709	0.24562	0.0640*
H11	0.04673	0.38302	0.08952	0.0840*
H12	0.11175	0.46428	−0.02770	0.0920*
H13	0.34110	0.52988	0.00955	0.0870*
H14	0.50947	0.51345	0.16372	0.0680*
H18	1.01463	0.37126	0.42275	0.0670*
H19	1.21761	0.28995	0.43119	0.0780*
H20	1.17047	0.17038	0.45289	0.0750*
H21	0.91735	0.13251	0.46387	0.0740*
H22	0.71184	0.21295	0.45224	0.0620*
HO1	0.061 (3)	0.4657 (15)	0.617 (2)	0.1190*
H23A	0.21254	0.42549	0.79796	0.1810*
H23B	0.07336	0.38048	0.73674	0.1810*
H23C	0.04282	0.45890	0.76915	0.1810*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0484 (6)	0.0509 (6)	0.0359 (6)	0.0044 (5)	0.0037 (5)	0.0042 (5)
N2	0.0646 (8)	0.0647 (8)	0.0388 (6)	0.0088 (6)	0.0142 (6)	0.0043 (5)
N3	0.0557 (7)	0.0551 (7)	0.0591 (8)	0.0089 (6)	0.0120 (6)	−0.0015 (6)
N4	0.0656 (9)	0.1250 (15)	0.0605 (9)	0.0014 (9)	0.0267 (8)	0.0042 (9)
N5	0.0602 (8)	0.0552 (8)	0.0845 (10)	−0.0080 (7)	−0.0053 (7)	−0.0160 (7)
C1	0.0707 (10)	0.0703 (10)	0.0390 (7)	0.0103 (8)	0.0004 (7)	0.0099 (7)
O1	0.0639 (7)	0.1204 (12)	0.0577 (7)	0.0139 (8)	0.0191 (6)	0.0105 (7)
C2	0.0933 (13)	0.0838 (12)	0.0428 (8)	0.0176 (10)	0.0161 (8)	0.0159 (8)
C3	0.0469 (7)	0.0407 (6)	0.0369 (6)	−0.0037 (5)	0.0067 (5)	−0.0032 (5)
C4	0.0432 (7)	0.0391 (6)	0.0373 (6)	−0.0009 (5)	0.0057 (5)	−0.0018 (5)
C5	0.0414 (6)	0.0390 (6)	0.0396 (6)	−0.0032 (5)	0.0067 (5)	0.0017 (5)
C6	0.0377 (6)	0.0438 (7)	0.0370 (6)	−0.0019 (5)	0.0051 (5)	−0.0007 (5)
C7	0.0397 (6)	0.0399 (6)	0.0400 (6)	−0.0044 (5)	0.0009 (5)	−0.0008 (5)
C8	0.0499 (7)	0.0397 (7)	0.0393 (6)	−0.0026 (6)	0.0076 (5)	−0.0017 (5)
C9	0.0451 (7)	0.0480 (7)	0.0381 (6)	0.0099 (6)	0.0095 (5)	0.0036 (5)
C10	0.0431 (7)	0.0721 (10)	0.0434 (7)	0.0063 (7)	0.0067 (6)	0.0015 (7)
C11	0.0436 (8)	0.1130 (15)	0.0509 (9)	0.0185 (9)	0.0027 (7)	−0.0113 (9)
C12	0.0699 (11)	0.1208 (16)	0.0386 (8)	0.0531 (12)	0.0064 (7)	0.0081 (9)
C13	0.0874 (13)	0.0836 (12)	0.0502 (9)	0.0394 (11)	0.0218 (9)	0.0238 (8)
C14	0.0666 (9)	0.0564 (9)	0.0501 (8)	0.0135 (7)	0.0182 (7)	0.0125 (7)
C15	0.0445 (7)	0.0657 (9)	0.0455 (7)	0.0031 (6)	0.0076 (6)	0.0017 (6)
C16	0.0407 (7)	0.0467 (7)	0.0466 (7)	0.0017 (6)	−0.0004 (5)	−0.0075 (6)
C17	0.0387 (6)	0.0444 (7)	0.0412 (7)	−0.0035 (5)	−0.0002 (5)	−0.0002 (5)
C18	0.0436 (7)	0.0490 (8)	0.0716 (10)	−0.0085 (6)	0.0034 (7)	0.0044 (7)
C19	0.0385 (7)	0.0712 (11)	0.0841 (12)	−0.0037 (7)	0.0074 (7)	0.0060 (9)
C20	0.0488 (8)	0.0629 (10)	0.0731 (11)	0.0106 (7)	0.0052 (7)	0.0055 (8)
C21	0.0582 (9)	0.0453 (8)	0.0798 (11)	0.0022 (7)	0.0080 (8)	0.0084 (7)
C22	0.0418 (7)	0.0462 (7)	0.0663 (9)	−0.0052 (6)	0.0053 (6)	0.0051 (6)
C23	0.0825 (15)	0.205 (3)	0.0758 (14)	−0.0012 (18)	0.0142 (12)	0.0563 (18)

Geometric parameters (Å, º)

N1—C1	1.4754 (18)	C17—C22	1.390 (2)
N1—C3	1.3710 (18)	C17—C18	1.387 (2)
N1—C7	1.4554 (17)	C18—C19	1.379 (2)
N2—C2	1.458 (2)	C19—C20	1.376 (3)
N2—C3	1.3453 (18)	C20—C21	1.376 (2)
N3—C8	1.1524 (19)	C21—C22	1.380 (2)
N4—C15	1.136 (2)	C1—H1A	0.9700
N5—C16	1.137 (2)	O1—HO1	0.92 (3)
C1—C2	1.517 (2)	C1—H1B	0.9700
O1—C23	1.375 (3)	C2—H2A	0.9700
N2—H2N	0.887 (18)	C2—H2B	0.9700
C3—C4	1.3753 (18)	C5—H5	0.9800
C4—C8	1.4029 (19)	C7—H7	0.9800
C4—C5	1.5151 (17)	C10—H10	0.9300
C5—C6	1.5687 (18)	C11—H11	0.9300
C5—C9	1.5177 (18)	C12—H12	0.9300
C6—C7	1.5720 (18)	C13—H13	0.9300
C6—C16	1.4770 (19)	C14—H14	0.9300
C6—C15	1.4767 (19)	C18—H18	0.9300
C7—C17	1.5091 (19)	C19—H19	0.9300
C9—C14	1.391 (2)	C20—H20	0.9300
C9—C10	1.386 (2)	C21—H21	0.9300
C10—C11	1.386 (2)	C22—H22	0.9300
C11—C12	1.380 (3)	C23—H23A	0.9600
C12—C13	1.370 (3)	C23—H23B	0.9600
C13—C14	1.378 (3)	C23—H23C	0.9600
C1—N1—C3	108.34 (11)	C17—C22—C21	120.35 (14)
C1—N1—C7	121.89 (12)	N1—C1—H1A	112.00
C3—N1—C7	118.49 (11)	N1—C1—H1B	112.00
C2—N2—C3	110.22 (13)	C2—C1—H1A	112.00
N1—C1—C2	101.20 (13)	C2—C1—H1B	112.00
N2—C2—C1	101.97 (14)	H1A—C1—H1B	109.00
C3—N2—H2N	123.9 (12)	C23—O1—HO1	105.2 (17)
C2—N2—H2N	122.3 (12)	N2—C2—H2B	111.00
N1—C3—C4	122.75 (12)	C1—C2—H2A	111.00
N2—C3—C4	127.72 (13)	C1—C2—H2B	111.00
N1—C3—N2	109.53 (12)	H2A—C2—H2B	109.00
C5—C4—C8	119.88 (11)	N2—C2—H2A	111.00
C3—C4—C5	121.27 (12)	C4—C5—H5	107.00
C3—C4—C8	118.52 (12)	C9—C5—H5	107.00
C6—C5—C9	113.12 (10)	C6—C5—H5	107.00
C4—C5—C9	113.71 (11)	N1—C7—H7	108.00
C4—C5—C6	108.31 (10)	C17—C7—H7	108.00
C5—C6—C15	108.86 (11)	C6—C7—H7	108.00
C5—C6—C16	111.67 (10)	C9—C10—H10	120.00

C7—C6—C16	109.34 (11)	C11—C10—H10	120.00
C15—C6—C16	108.80 (11)	C12—C11—H11	120.00
C7—C6—C15	109.63 (11)	C10—C11—H11	120.00
C5—C6—C7	108.52 (10)	C11—C12—H12	120.00
C6—C7—C17	113.94 (11)	C13—C12—H12	120.00
N1—C7—C6	105.90 (10)	C14—C13—H13	120.00
N1—C7—C17	112.68 (11)	C12—C13—H13	120.00
N3—C8—C4	178.94 (14)	C9—C14—H14	120.00
C10—C9—C14	118.99 (13)	C13—C14—H14	120.00
C5—C9—C10	122.00 (12)	C19—C18—H18	120.00
C5—C9—C14	119.01 (13)	C17—C18—H18	120.00
C9—C10—C11	120.11 (15)	C18—C19—H19	120.00
C10—C11—C12	119.91 (16)	C20—C19—H19	120.00
C11—C12—C13	120.48 (16)	C21—C20—H20	120.00
C12—C13—C14	119.84 (18)	C19—C20—H20	120.00
C9—C14—C13	120.66 (17)	C20—C21—H21	120.00
N4—C15—C6	178.24 (18)	C22—C21—H21	120.00
N5—C16—C6	178.13 (16)	C17—C22—H22	120.00
C7—C17—C18	118.34 (12)	C21—C22—H22	120.00
C18—C17—C22	118.52 (13)	O1—C23—H23A	109.00
C7—C17—C22	123.14 (12)	O1—C23—H23B	109.00
C17—C18—C19	120.67 (14)	O1—C23—H23C	109.00
C18—C19—C20	120.48 (15)	H23A—C23—H23B	109.00
C19—C20—C21	119.31 (15)	H23A—C23—H23C	109.00
C20—C21—C22	120.66 (14)	H23B—C23—H23C	109.00

C3—N1—C1—C2	26.59 (16)	C9—C5—C6—C7	−179.03 (10)
C7—N1—C1—C2	169.55 (13)	C9—C5—C6—C15	61.71 (14)
C7—N1—C3—N2	−158.46 (12)	C4—C5—C6—C15	−171.28 (11)
C1—N1—C7—C6	171.10 (12)	C16—C6—C7—N1	−57.45 (13)
C1—N1—C3—N2	−14.05 (16)	C16—C6—C7—C17	66.96 (14)
C3—N1—C7—C17	−174.68 (11)	C15—C6—C7—C17	−52.24 (15)
C1—N1—C3—C4	166.57 (13)	C5—C6—C7—N1	64.58 (12)
C7—N1—C3—C4	22.16 (19)	C5—C6—C7—C17	−171.02 (10)
C1—N1—C7—C17	45.91 (17)	C15—C6—C7—N1	−176.64 (11)
C3—N1—C7—C6	−49.49 (14)	N1—C7—C17—C18	−137.73 (13)
C3—N2—C2—C1	22.03 (17)	N1—C7—C17—C22	42.12 (18)
C2—N2—C3—C4	173.60 (14)	C6—C7—C17—C18	101.58 (15)
C2—N2—C3—N1	−5.74 (17)	C6—C7—C17—C22	−78.57 (16)
N1—C1—C2—N2	−28.10 (16)	C5—C9—C10—C11	−179.63 (15)
N1—C3—C4—C5	−8.3 (2)	C14—C9—C10—C11	1.2 (2)
N1—C3—C4—C8	178.32 (12)	C5—C9—C14—C13	−179.97 (16)
N2—C3—C4—C5	172.44 (13)	C10—C9—C14—C13	−0.8 (2)
N2—C3—C4—C8	−0.9 (2)	C9—C10—C11—C12	−0.8 (3)
C3—C4—C5—C6	24.53 (16)	C10—C11—C12—C13	−0.1 (3)
C8—C4—C5—C6	−162.18 (11)	C11—C12—C13—C14	0.6 (3)
C8—C4—C5—C9	−35.51 (17)	C12—C13—C14—C9	−0.1 (3)
C3—C4—C5—C9	151.19 (12)	C7—C17—C18—C19	179.89 (15)

C4—C5—C6—C7	−52.02 (13)	C22—C17—C18—C19	0.0 (2)
C9—C5—C6—C16	−58.43 (14)	C7—C17—C22—C21	−179.19 (14)
C4—C5—C9—C10	−43.99 (18)	C18—C17—C22—C21	0.7 (2)
C4—C5—C9—C14	135.18 (14)	C17—C18—C19—C20	−0.6 (3)
C6—C5—C9—C10	80.12 (16)	C18—C19—C20—C21	0.5 (3)
C6—C5—C9—C14	−100.71 (15)	C19—C20—C21—C22	0.2 (3)
C4—C5—C6—C16	68.57 (13)	C20—C21—C22—C17	−0.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H*O*1···N3^{i}	0.92 (3)	2.02 (3)	2.907 (2)	161 (2)
N2—H2*N*···O1	0.887 (18)	2.004 (18)	2.870 (2)	165.0 (16)
C7—H7···N3^{ii}	0.98	2.52	3.3742 (19)	146

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