

Crystal structure and Hirshfeld surface analysis of dimethyl 5-[2-(2,4,6-trioxo-1,3-diazinan-5-ylidene)hydrazin-1-yl]benzene-1,3-dicarboxylate 0.224-hydrate

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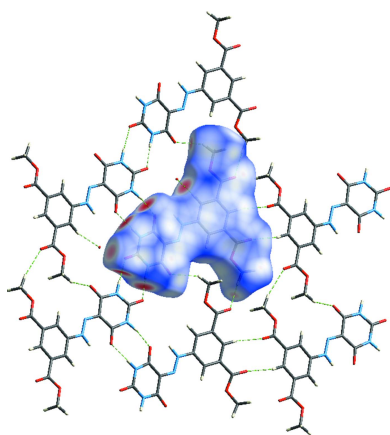
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In the crystal, the whole molecule of the title compound, C₁₄H₁₂N₄O₇·0.224H₂O, is nearly planar with a maximum deviation from the least-squares plane of 0.352 (1) Å. The molecular conformation is stabilized by an intramolecular N—H···O hydrogen bond, generating an *S*(6) ring motif. In the crystal, molecules are linked by centrosymmetric pairs of N—H···O hydrogen bonds, forming ribbons along the *c*-axis direction. These ribbons connected by van der Waals contacts, forming sheets parallel to the *ac* plane. There are also intermolecular van der Waals contacts and C—H··· π interactions between the sheets. A Hirshfeld surface analysis indicates that the most prevalent interactions are O···H/H···O (41.2%), H···H (19.2%), C···H/H···C (12.2%) and C···O/O···C (8.4%).

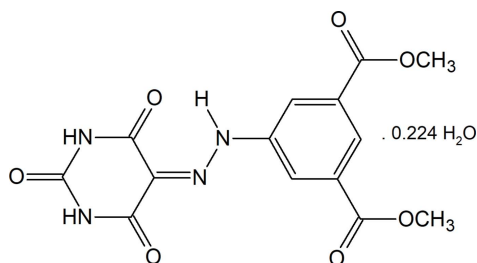
1. Chemical context

Arylhydrazones, besides their biological significance (Viswanathan *et al.*, 2019), can also be used as precursors in the synthesis of coordination compounds (Gurbanov *et al.*, 2017, 2018*a,b*; Ma *et al.*, 2017*a,b*) and as building blocks in the construction of supramolecular structures owing to their hydrogen-bond donor and acceptor capabilities (Mahmoudi *et al.*, 2016, 2017*a,b,c*, 2018*a,b*; 2019). All the reported hydrazone ligands are stabilized in the hydrazone form by intramolecular resonance-assisted hydrogen bonding (RAHB) between the hydrazone =N—NH— fragment and the carbonyl group, giving a six-membered ring (Gurbanov *et al.*, 2020*a*; Kopylovich *et al.*, 2011*a,b*; Mizar *et al.*, 2012). The use of multifunctional ligands in coordination chemistry is a common way to increase the water solubility of metal complexes, which is important for catalytic applications in aqueous medium (Ma *et al.*, 2020, 2021; Mahmudov *et al.*, 2013; Sutradhar *et al.*, 2015, 2016). Moreover, non-covalent interactions such as hydrogen, halogen and chalcogen bonds as well as π -interactions or their cooperation are able to contribute to synthesis and catalysis and improve the properties of materials (Gurbanov *et al.*, 2020*b*; Karmakar *et al.*, 2017; Khalilov *et al.*, 2018*a,b*; MacLeod *et al.*, 2012; Shikhaliyev *et al.*, 2019; Shixaliyev *et al.*, 2014). For that, the main skeleton of the hydrazone ligand should be decorated by non-covalent bond donor centre(s). In



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a continuation of our work in this area, we have prepared a new hydrazone ligand, dimethyl 5-[2-[2,4,6-trioxotetrahydropyrimidin-5(2*H*)-ylidene] hydrazineyl]isophthalate, which provides the centres for coordination and intermolecular non-covalent interactions.



2. Structural commentary

The asymmetric unit of the title structure contains one title molecule and a water molecule, which partially occupies a small cavity with an occupancy factor of 0.224 (5). The title molecule (Fig. 1) is nearly planar with the largest deviation from the least-squares plane being 0.352 (1) Å for the methylcarboxylate atom O6. The 1,3-diazinane ring makes a dihedral angle of 9.96 (5)° with the benzene ring. The planar molecular conformation is stabilized by an intramolecular N—H···O contact (Table 1), generating an *S*(6) ring motif (Bernstein *et al.*, 1995).

3. Supramolecular features

In the crystal, the molecules are linked by pairs of N—H···O hydrogen bonds into ribbons along the *c*-axis direction (Table 1). These ribbons are connected by van der Waals interactions, forming sheets parallel to the *ac* plane. There are

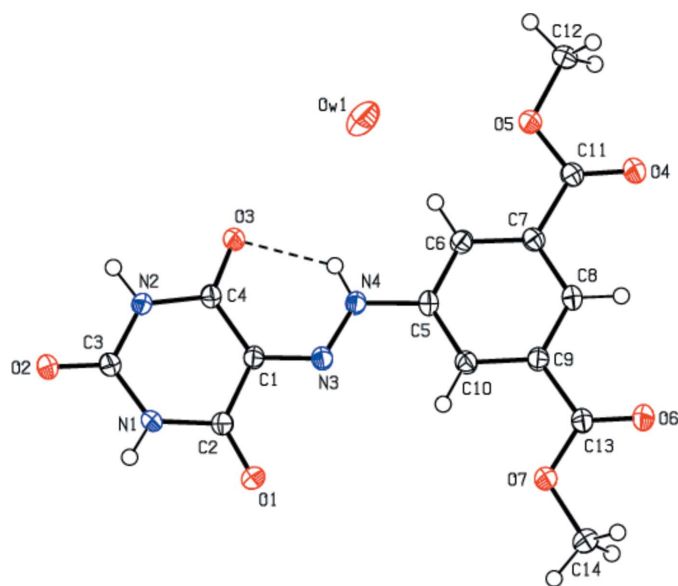


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level.

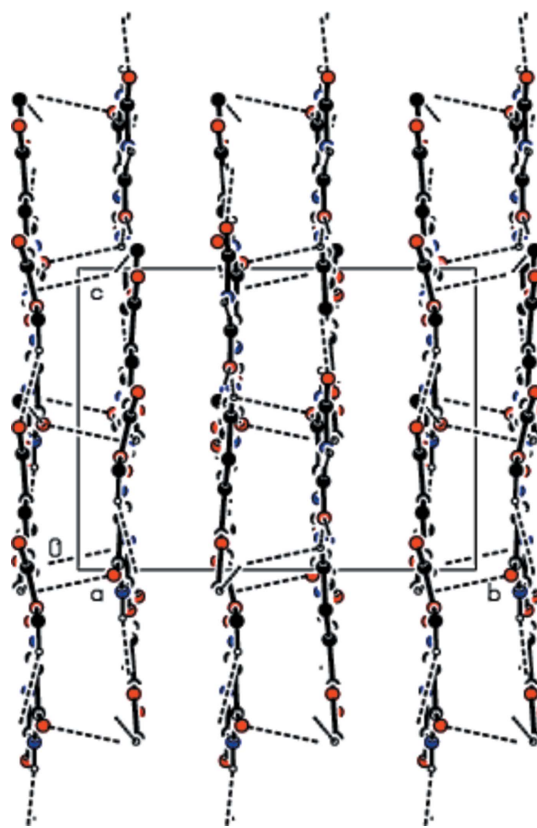


Figure 2
A view down the *a* axis showing the intermolecular contacts forming the layered structure.

also other van der Waals contacts and C—H··· π interactions between the sheets (Table 2), consolidating the crystal packing (Figs. 2–4).

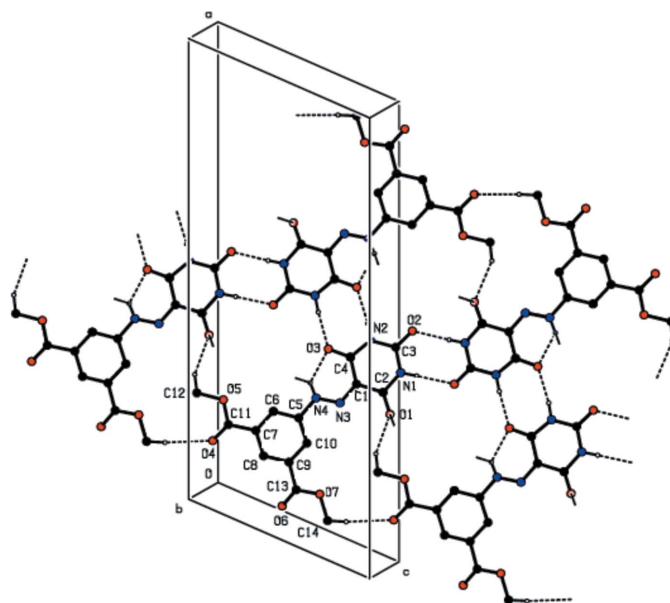


Figure 3
A view of intermolecular hydrogen bonds forming the ribbons along the *c*-axis direction.

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

Cg2 is the centroid of the C5–C10 benzene ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1N \cdots O2 ⁱ	0.86	2.03	2.8800 (13)	174
N2–H2N \cdots O3 ⁱⁱ	0.90	2.01	2.8931 (15)	168
N4–H4N \cdots O3	0.86	2.02	2.6571 (15)	131
C6–H6 \cdots Ow1	0.95	2.14	3.061 (6)	163
C12–H12B \cdots O1 ⁱⁱⁱ	0.98	2.39	3.2743 (17)	149
C14–H14B \cdots O4 ^{iv}	0.98	2.53	3.4754 (16)	163
C12–H12C \cdots Cg2 ^v	0.98	2.73	3.4717 (15)	133

Symmetry codes: (i) $-x+1, y, -z+\frac{5}{2}$; (ii) $-x+1, y, -z+\frac{3}{2}$; (iii) $x, y, z-1$; (iv) $x, y, z+1$; (v) $x, -y+1, z-\frac{1}{2}$.

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

Contact	Distance	Symmetry operation
O1 \cdots *Ow1	3.129	$x, y, 1+z$
O1 \cdots H12B	2.39	$x, y, 1+z$
O1 \cdots H4N	2.59	$x, 1-y, \frac{1}{2}+z$
H12A \cdots O1	2.67	$\frac{1}{2}-x, \frac{1}{2}-y, 1-z$
H1N \cdots O2	2.03	$1-x, y, \frac{3}{2}-z$
O2 \cdots *Ow1	2.662	$1-x, y, \frac{3}{2}-z$
N2 \cdots O2	3.226	$1-x, 1-y, 2-z$
O2 \cdots H14C	2.64	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
H2N \cdots O3	2.01	$1-x, y, \frac{3}{2}-z$
H4N \cdots O1	2.59	$x, 1-y, -\frac{1}{2}+z$
H12B \cdots O1	2.39	$x, y, -1+z$
H8 \cdots O6	2.66	$-x, y, \frac{1}{2}-z$
H14A \cdots O6	2.67	$-x, 1-y, 1-z$
H14C \cdots O2	2.64	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
C1 \cdots *Ow1	3.297	$x, 1-y, \frac{1}{2}+z$
H6 \cdots *Ow1	2.14	x, y, z
H12B \cdots C12	3.10	$\frac{1}{2}-x, \frac{1}{3}-y, -z$
H14B \cdots C14	2.93	$-x, y, \frac{2}{3}-z$
H12A \cdots *Ow1	2.70	$\frac{1}{2}-x, \frac{1}{2}-y, -z$

*Ow1 indicates the oxygen atom of the water molecule with an occupancy of 0.224 (5).

4. Hirshfeld surface analysis

The Hirshfeld surface for the title molecule was performed and its associated two-dimensional fingerprint plots were prepared using *Crystal Explorer 17* (Turner *et al.*, 2017) to further investigate the intermolecular interactions in the title structure. The oxygen atom of the water molecule with partial occupancy was not taken into account. The Hirshfeld surface mapped over d_{norm} with corresponding colours representing intermolecular interactions is shown in Fig. 5. The red spots on the surface correspond to the N–H \cdots O and C–H \cdots O

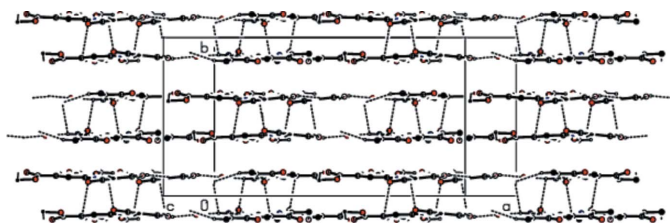


Figure 4
A view of the projection on the ab plane showing the contacts between layers.

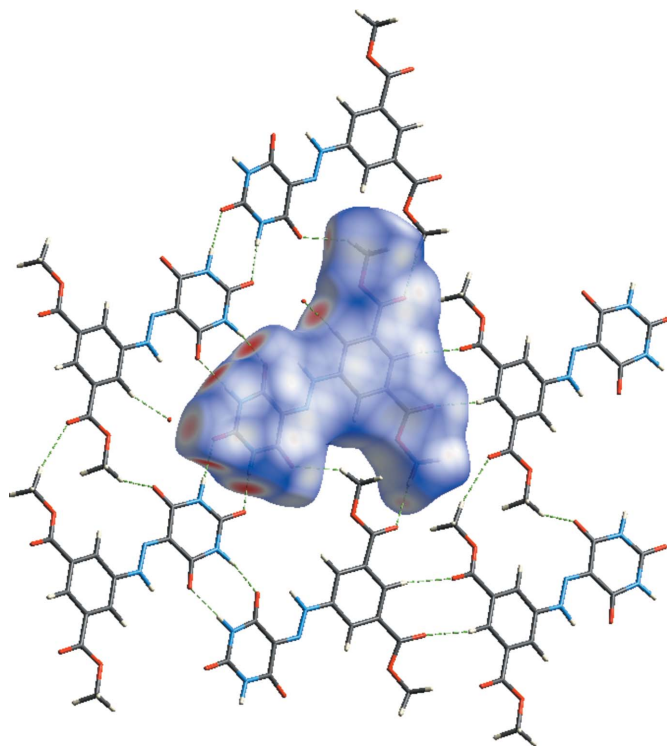


Figure 5
A view of the Hirshfeld surface mapped over d_{norm} , with interactions to neighbouring molecules shown as green dashed lines.

interactions (Tables 1 and 2). The Hirshfeld surface mapped over electrostatic potential (Spackman *et al.*, 2009) is shown in Fig. 6. The blue regions indicate positive electrostatic potential

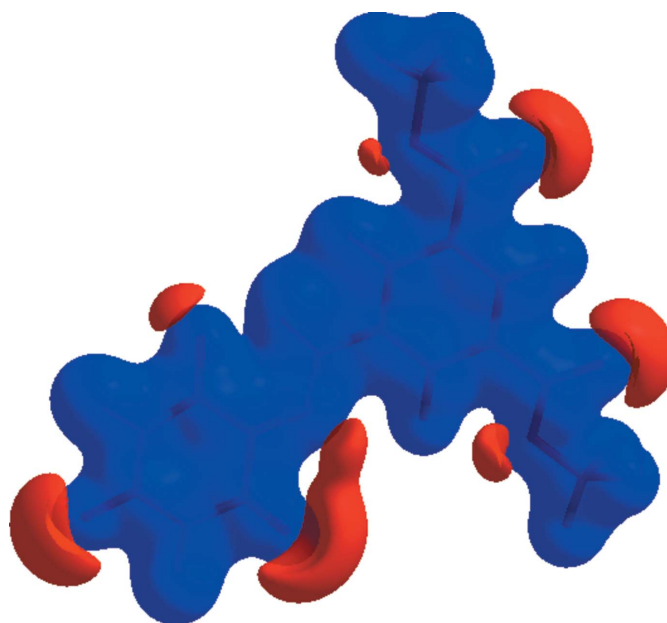


Figure 6
The Hirshfeld surface of the title compound plotted over electrostatic potential energy in the range from -0.0500 to 0.0500 a.u. using the STO-3G basis set at the Hartree-Fock level of theory. Hydrogen-bond donors and acceptors are shown as blue and red regions around the atoms, corresponding to positive and negative potentials, respectively.

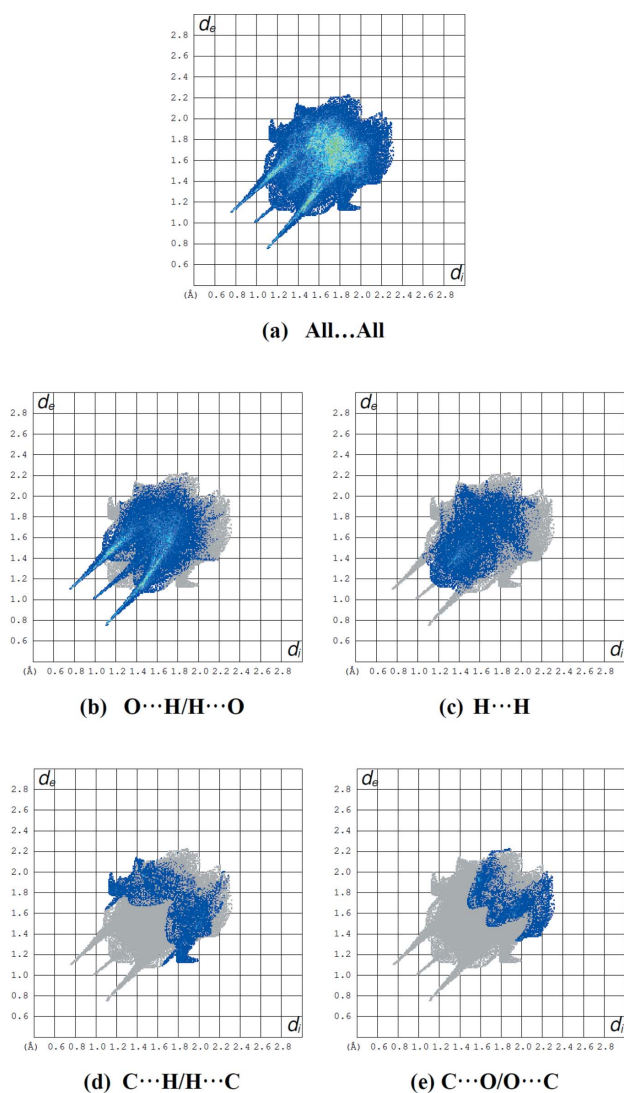


Figure 7
The two-dimensional fingerprint plots of the title compound, showing (a) all interactions, and delineated into (b) $O\cdots H/H\cdots O$, (c) $H\cdots H$, (d) $C\cdots H/H\cdots C$ and (e) $C\cdots O/O\cdots C$, interactions [d_e and d_i represent the distances from a point on the Hirshfeld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

(hydrogen-bond donors), while the red regions indicate negative electrostatic potential (hydrogen-bond acceptors). The two-dimensional fingerprint plots (McKinnon *et al.*, 2007) are shown in Fig. 7. $O\cdots H/H\cdots O$ contacts make the largest contribution (41.2%; Fig. 7b) to the Hirshfeld surface. The other large contributions to the Hirshfeld surface are from $H\cdots H$ (19.2%; Fig. 7c), $C\cdots H/H\cdots C$ (12.2%; Fig. 7d) and $C\cdots O/O\cdots C$ (8.4%; Fig. 7e) interactions. All contributions to the Hirshfeld surface are listed in Table 3. These interactions play a crucial role in the overall cohesion of the crystal packing.

5. Database survey

A search of Cambridge Crystallographic Database (CSD, version 5.40, update of September 2019; Groom *et al.*, 2016)

Table 3

Percentage contributions of interatomic contacts to the Hirshfeld surface for the title compound.

Contact	Percentage contribution
$O\cdots H/H\cdots O$	41.2
$H\cdots H$	19.2
$C\cdots H/H\cdots C$	12.2
$C\cdots O/O\cdots C$	8.4
$O\cdots O$	5.6
$N\cdots O/O\cdots N$	4.7
$C\cdots N/N\cdots C$	3.2
$C\cdots C$	2.8
$N\cdots H/H\cdots N$	2.7

was undertaken for structures containing the 5-(2-methylhydrazinylidene)-1,3-diazinane moiety. The first three structures are free bases are: 2-[2-[(1*H*-imidazol-5-yl)methylidene]-1-methylhydrazinyl]pyridine (QUGVEW; Bocian *et al.*, 2020), 2-[2-[(1*H*-imidazol-2-yl)methylidene]-1-methylhydrazinyl]-1*H*-benzimidazole monohydrate (QUGVIA; Bocian *et al.*, 2020) and 2-[1-methyl-2-[(1-methyl-1*H*-imidazol-2-yl)methylidene]hydrazinyl]-1*H*-benzimidazole hydrate unknown solvate (QUGVOG; Bocian *et al.*, 2020). The other two are triflate salts are: 5-[[2-(1*H*-benzimidazol-2-yl)-2-methylhydrazinylidene]methyl]-1*H*-imidazol-3-ium trifluoromethanesulfonate monohydrate (QUGVUM; Bocian *et al.*, 2020) and (2-[2-[(1*H*-imidazol-3-ium-2-yl)methylene]-1-methylhydrazinyl]pyridin-1-ium) bis(trifluoromethanesulfonate) (QUGWAT; Bocian *et al.*, 2020).

In the structures of QUGVEW, QUGVIA, QUGVOG, QUGVUM and QUGWAT, the most important contribution to the stabilization of the crystal packing is provided by π - π interactions, especially between cations in the structures of salts, while the characteristics of the crystal architecture are influenced by directional interactions, especially relatively strong hydrogen bonds. In one of the structures (QUGWAT), an interesting example of a non-typical $F\cdots O$ interaction was found whose length, 2.859 (2) Å, is one of the shortest ever reported.

6. Synthesis and crystallization

Diazotization: 2.09 g (10 mmol) of dimethyl 5-aminoisophthalate were dissolved in 50 mL of water, the solution was cooled on an ice bath to 273 K and 0.69 g (10 mmol) of NaNO_2 were added; 2.00 mL of HCl were then added in 0.5 mL portions over 1 h. The temperature of the mixture should not exceed 278 K.

Azocoupling: NaOH (0.40 g, 10 mmol) was added to a mixture of 10 mmol (1.28 g) of barbituric acid with 25.00 mL of water. The solution was cooled on an ice bath and a suspension of 3,5-bis(methoxycarbonyl)benzenediazonium chloride, prepared according to the procedure described above, was added in two equal portions under vigorous stirring for 1 h. The formed precipitate of the title compound was filtered off, recrystallized from methanol and dried in air.

Table 4
Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₁₂ N ₄ O ₇ ·0.224H ₂ O
<i>M</i> _r	351.86
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	24.2097 (11), 12.6311 (6), 10.4022 (5)
β (°)	113.133 (2)
<i>V</i> (Å ³)	2925.2 (2)
<i>Z</i>	8
Radiation type	Mo Kα
μ (mm ⁻¹)	0.13
Crystal size (mm)	0.34 × 0.32 × 0.27
Data collection	
Diffraction	Bruker APEXII CCD
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	34832, 2944, 2699
<i>R</i> _{int}	0.017
(sin θ/λ) _{max} (Å ⁻¹)	0.625
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.034, 0.102, 1.04
No. of reflections	2944
No. of parameters	241
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.29, -0.21

Computer programs: APEX2 and SAINT (Bruker, 2007), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2020).

Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution.

The title compound: Yield, 68% (based on barbituric acid), yellow powder soluble in DMSO, methanol, ethanol and DMF. Analysis calculated for C₁₄H₁₂N₄O₇ (*M*_r = 348.27): C, 48.28; H, 3.47; N, 16.09; found: C, 48.25; H, 3.41; N, 16.03%. ESI-MS: *m/z*: 349.2 [*M*_r + H]⁺. IR (KBr): 3160, 3090 and 2846 ν(NH), 1745 and 1663 ν(C=O), 1610 ν(C=O···H) cm⁻¹. ¹H NMR (300.130 MHz) in DMSO-*d*₆, internal TMS, δ (ppm): 8.20–8.36 (3H, Ar–H), 11.32 (*s*, 1H, N–H), 11.54 (*s*, 1H, N–H), 14.08 (*s*, 1H, N–H). ¹³C{¹H} NMR (75.468 MHz, DMSO-*d*₆): δ: 55.6 (2OCH₃), 119.54 (2Ar–H), 121.8 (Ar–H), 127.4 (2C–COOCH₃), 133.25 (C=N), 142.87 (C–NHN=), 150.24 (C=O), 160.32 (C=O), 161.90 (C=O···H) and 166.56 (2COOCH₃).

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 4. The H atoms of the NH groups were located by difference Fourier synthesis and their coordinates were fixed. All C-bound H atoms were positioned geometrically and refined using a riding model, with C–H = 0.95 and 0.98 Å, and with *U*_{iso}(H) = 1.2 or 1.5*U*_{eq}(C). There is a small cavity in the crystal, which is only partially occupied by a water molecule, with an occupancy of 0.224 (5), and its hydrogen atoms could not be located.

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The authors' contributions are as follows. Conceptualization, ZA, MA, GZM, FEH, SRH, NTS, and AB; methodology, SRH, and NTS; investigation, ZA, and GZM; writing (original draft), FEH, MA and AB; writing (review and editing of the manuscript), MA and AB; crystal-structure determination, GZM; visualization, ZA, and MA; funding acquisition, GZM, FEH, SRH, and NTS; resources, ZA, MA and AB; supervision, MA and AB.

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References

- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bocian, A., Górczyński, A., Marcinkowski, D., Dutkiewicz, G., Patroniak, V. & Kubicki, M. (2020). *Acta Cryst. C* **76**, 367–374.
- Bruker (2007). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- 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.
- Gurbanov, A. V., Kuznetsov, M. L., Demukhamedova, S. D., Alieva, I. N., Godjaev, N. M., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2020a). *CrystEngComm*, **22**, 628–633.
- Gurbanov, A. V., Kuznetsov, M. L., Mahmudov, K. T., Pombeiro, A. J. L. & Resnati, G. (2020b). *Chem. Eur. J.* **26**, 14833–14837.
- Gurbanov, A. V., Maharramov, A. M., Zubkov, F. I., Saifutdinov, A. M. & Guseinov, F. I. (2018a). *Aust. J. Chem.* **71**, 190–194.
- Gurbanov, A. V., Mahmoudi, G., Guedes da Silva, M. F. C., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2018b). *Inorg. Chim. Acta*, **471**, 130–136.
- Gurbanov, A. V., Mahmudov, K. T., Sutradhar, M., Guedes da Silva, F. C., Mahmudov, T. A., Guseinov, F. I., Zubkov, F. I., Maharramov, A. M. & Pombeiro, A. J. L. (2017). *J. Organomet. Chem.* **834**, 22–27.
- Karmakar, A., Rúbio, G. M. D. M., Paul, A., Guedes da Silva, M. F. C., Mahmudov, K. T., Guseinov, F. I., Carabineiro, S. A. C. & Pombeiro, A. J. L. (2017). *Dalton Trans.* **46**, 8649–8657.
- Khalilov, A. N., Asgarova, A. R., Gurbanov, A. V., Maharramov, A. M., Nagiyev, F. N. & Brito, I. (2018a). *Z. Kristallogr. New Cryst. Struct.* **233**, 1019–1020.
- Khalilov, A. N., Asgarova, A. R., Gurbanov, A. V., Nagiyev, F. N. & Brito, I. (2018b). *Z. Kristallogr. New Cryst. Struct.* **233**, 947–948.
- Kopylovich, M. N., Mahmudov, K. T., Haukka, M., Luzyanin, K. V. & Pombeiro, A. J. L. (2011a). *Inorg. Chim. Acta*, **374**, 175–180.
- Kopylovich, M. N., Mahmudov, K. T., Mizar, A. & Pombeiro, A. J. L. (2011b). *Chem. Commun.* **47**, 7248–7250.
- Ma, Z., Gurbanov, A. V., Maharramov, A. M., Guseinov, F. I., Kopylovich, M. N., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2017a). *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. (2017b). *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.
- Mac Leod, T. C. O., Kopylovich, M. N., Guedes da Silva, M. F. C., Mahmudov, K. T. & Pombeiro, A. J. L. (2012). *Appl. Catal. Gen.* **439–440**, 15–23.

- Mahmoudi, G., Bauzá, A., Gurbanov, A. V., Zubkov, F. I., Maniukiewicz, W., Rodríguez-Diéguez, A., López-Torres, E. & Frontera, A. (2016). *CrystEngComm*, **18**, 9056–9066.
- Mahmoudi, G., Dey, L., Chowdhury, H., Bauzá, A., Ghosh, B. K., Kirillov, A. M., Seth, S. K., Gurbanov, A. V. & Frontera, A. (2017a). *Inorg. Chim. Acta*, **461**, 192–205.
- Mahmoudi, G., Gurbanov, A. V., Rodríguez-Hermida, S., Carballo, R., Amini, M., Bacchi, A., Mitoraj, M. P., Sagan, F., Kukulka, M. & Safin, D. A. (2017b). *Inorg. Chem.* **56**, 9698–9709.
- 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.
- Mahmoudi, G., Seth, S. K., Bauzá, A., Zubkov, F. I., Gurbanov, A. V., White, J., Stilinović, V., Doert, T. & Frontera, A. (2018a). *CrystEngComm*, **20**, 2812–2821.
- Mahmoudi, G., Zangrando, E., Mitoraj, M. P., Gurbanov, A. V., Zubkov, F. I., Moosavifar, M., Konyaeva, I. A., Kirillov, A. M. & Safin, D. A. (2018b). *New J. Chem.* **42**, 4959–4971.
- Mahmoudi, G., Zaręba, J. K., Gurbanov, A. V., Bauzá, A., Zubkov, F. I., Kubicki, M., Stilinović, V., Kinzhybalov, V. & Frontera, A. (2017c). *Eur. J. Inorg. Chem.* pp. 4763–4772.
- Mahmudov, K. T., Kopylovich, M. N., Haukka, M., Mahmudova, G. S., Esmaila, E. F., Chyragov, F. M. & Pombeiro, A. J. L. (2013). *J. Mol. Struct.* **1048**, 108–112.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
- Mizar, A., Guedes da Silva, M. F. C., Kopylovich, M. N., Mukherjee, S., Mahmudov, K. T. & Pombeiro, A. J. L. (2012). *Eur. J. Inorg. Chem.* pp. 2305–2313.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Shikhaliyev, N. Q., Kuznetsov, M. L., Maharramov, A. M., Gurbanov, A. V., Ahmadova, N. E., Nenajdenko, V. G., Mahmudov, K. T. & Pombeiro, A. J. L. (2019). *CrystEngComm*, **21**, 5032–5038.
- Shixaliyev, N. Q., Gurbanov, A. V., Maharramov, A. M., Mahmudov, K. T., Kopylovich, M. N., Martins, L. M. D. R. S., Muzalevskiy, V. M., Nenajdenko, V. G. & Pombeiro, A. J. L. (2014). *New J. Chem.* **38**, 4807–4815.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Sutradhar, M., Alegria, E. C. B. A., Mahmudov, K. T., Guedes da Silva, M. F. C. & Pombeiro, A. J. L. (2016). *RSC Adv.* **6**, 8079–8088.
- Sutradhar, M., Martins, L. M. D. R. S., Guedes da Silva, M. F. C., Mahmudov, K. T., Liu, C.-M. & Pombeiro, A. J. L. (2015). *Eur. J. Inorg. Chem.* pp. 3959–3969.
- Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *Crystal Explorer 17*. The University of Western Australia.
- Viswanathan, A., Kute, D., Musa, A., Mani, S. K., Sipilä, V., Emmert-Streib, F., Zubkov, F. I., Gurbanov, A. V., Yli-Harja, O. & Kandhavelu, M. (2019). *Eur. J. Med. Chem.* **166**, 291–303.

supporting information

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Crystal structure and Hirshfeld surface analysis of dimethyl 5-[2-(2,4,6-trioxo-1,3-diazinan-5-ylidene)hydrazin-1-yl]benzene-1,3-dicarboxylate 0.224-hydrate

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Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

Dimethyl 5-[2-(2,4,6-trioxo-1,3-diazinan-5-ylidene)hydrazin-1-yl]benzene-1,3-dicarboxylate 0.224-hydrate

Crystal data

$C_{14}H_{12}N_4O_7 \cdot 0.224H_2O$
 $M_r = 351.86$
 Monoclinic, *C2/c*
 $a = 24.2097$ (11) Å
 $b = 12.6311$ (6) Å
 $c = 10.4022$ (5) Å
 $\beta = 113.133$ (2)°
 $V = 2925.2$ (2) Å³
 $Z = 8$

$F(000) = 1454$
 $D_x = 1.598$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9840 reflections
 $\theta = 3.2$ – 26.4 °
 $\mu = 0.13$ mm⁻¹
 $T = 150$ K
 Block, orange
 $0.34 \times 0.32 \times 0.27$ mm

Data collection

Bruker APEXII CCD
 diffractometer
 φ and ω scans
 34832 measured reflections
 2944 independent reflections
 2699 reflections with $I > 2\sigma(I)$

$R_{int} = 0.017$
 $\theta_{max} = 26.4$ °, $\theta_{min} = 3.2$ °
 $h = -30 \rightarrow 30$
 $k = -15 \rightarrow 15$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.102$
 $S = 1.04$
 2944 reflections
 241 parameters
 6 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 2.1077P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.29$ e Å⁻³
 $\Delta\rho_{min} = -0.21$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.37057 (5)	0.39423 (9)	0.82909 (12)	0.0190 (2)	
C2	0.37833 (5)	0.39902 (9)	0.97648 (12)	0.0207 (2)	
C3	0.48693 (5)	0.37742 (9)	1.04270 (12)	0.0208 (2)	
C4	0.42279 (5)	0.38365 (8)	0.79361 (12)	0.0186 (2)	
C5	0.24165 (5)	0.38344 (8)	0.50833 (12)	0.0192 (2)	
C6	0.23130 (5)	0.37794 (9)	0.36716 (12)	0.0204 (2)	
H6	0.263906	0.380695	0.338172	0.025*	
C7	0.17254 (5)	0.36834 (9)	0.26874 (11)	0.0197 (2)	
C8	0.12459 (5)	0.36539 (9)	0.31079 (12)	0.0201 (2)	
H8	0.084612	0.358679	0.243355	0.024*	
C9	0.13569 (5)	0.37237 (9)	0.45277 (12)	0.0200 (2)	
C10	0.19423 (5)	0.38111 (9)	0.55282 (12)	0.0203 (2)	
H10	0.201704	0.385399	0.649417	0.024*	
C11	0.15859 (5)	0.35937 (9)	0.11562 (12)	0.0211 (2)	
C12	0.19700 (5)	0.35182 (11)	-0.05977 (12)	0.0264 (3)	
H12A	0.177183	0.284238	-0.096410	0.040*	
H12B	0.235389	0.355077	-0.070599	0.040*	
H12C	0.171209	0.410245	-0.111573	0.040*	
C13	0.08236 (5)	0.37078 (10)	0.49220 (12)	0.0231 (3)	
C14	0.04671 (6)	0.39831 (12)	0.66992 (14)	0.0307 (3)	
H14A	0.022390	0.461429	0.630597	0.046*	
H14B	0.062181	0.401216	0.772194	0.046*	
H14C	0.021864	0.334851	0.636695	0.046*	
N1	0.43716 (4)	0.38898 (8)	1.07229 (10)	0.0215 (2)	
H1N	0.445330	0.388946	1.160377	0.026 (4)*	
N2	0.47752 (4)	0.37483 (8)	0.90340 (10)	0.0209 (2)	
H2N	0.510968	0.367522	0.886519	0.032 (4)*	
N3	0.31416 (4)	0.39456 (7)	0.73771 (10)	0.0197 (2)	
N4	0.30173 (4)	0.38952 (8)	0.60489 (10)	0.0202 (2)	
H4N	0.329280	0.391432	0.572748	0.041 (5)*	
O1	0.33809 (4)	0.41106 (8)	1.01707 (9)	0.0285 (2)	
O2	0.53768 (4)	0.37191 (8)	1.13392 (9)	0.0279 (2)	
O3	0.41946 (4)	0.38163 (7)	0.67172 (8)	0.0229 (2)	
O4	0.10827 (4)	0.35077 (8)	0.02776 (9)	0.0310 (2)	
O5	0.20773 (4)	0.36060 (7)	0.08791 (8)	0.0250 (2)	
O6	0.03258 (4)	0.35068 (10)	0.41153 (10)	0.0431 (3)	
O7	0.09668 (4)	0.39450 (8)	0.62583 (9)	0.0292 (2)	
OW1	0.3463 (2)	0.3484 (4)	0.3151 (6)	0.0466 (19)	0.224 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0158 (5)	0.0212 (5)	0.0187 (5)	-0.0008 (4)	0.0054 (4)	-0.0001 (4)
C2	0.0184 (5)	0.0233 (6)	0.0203 (6)	-0.0022 (4)	0.0074 (5)	-0.0026 (4)
C3	0.0192 (5)	0.0237 (6)	0.0179 (5)	0.0009 (4)	0.0054 (4)	-0.0003 (4)
C4	0.0166 (5)	0.0198 (5)	0.0175 (5)	-0.0002 (4)	0.0047 (4)	0.0010 (4)
C5	0.0157 (5)	0.0195 (5)	0.0193 (5)	-0.0003 (4)	0.0034 (4)	0.0016 (4)
C6	0.0188 (5)	0.0220 (5)	0.0209 (6)	0.0006 (4)	0.0081 (4)	0.0018 (4)
C7	0.0203 (5)	0.0198 (5)	0.0177 (6)	0.0005 (4)	0.0061 (4)	0.0010 (4)
C8	0.0171 (5)	0.0211 (5)	0.0189 (5)	-0.0002 (4)	0.0034 (4)	0.0003 (4)
C9	0.0173 (5)	0.0223 (5)	0.0193 (5)	-0.0007 (4)	0.0061 (4)	0.0006 (4)
C10	0.0197 (5)	0.0229 (5)	0.0172 (5)	-0.0006 (4)	0.0061 (4)	0.0006 (4)
C11	0.0210 (5)	0.0222 (5)	0.0192 (5)	0.0008 (4)	0.0070 (4)	0.0011 (4)
C12	0.0253 (6)	0.0365 (7)	0.0180 (6)	0.0003 (5)	0.0092 (5)	0.0008 (5)
C13	0.0185 (6)	0.0295 (6)	0.0192 (5)	-0.0006 (4)	0.0053 (4)	0.0002 (4)
C14	0.0221 (6)	0.0462 (8)	0.0262 (6)	-0.0023 (5)	0.0121 (5)	-0.0036 (5)
N1	0.0184 (5)	0.0310 (5)	0.0141 (5)	-0.0001 (4)	0.0054 (4)	-0.0023 (4)
N2	0.0149 (5)	0.0304 (5)	0.0167 (5)	0.0025 (4)	0.0056 (4)	0.0005 (4)
N3	0.0174 (5)	0.0219 (5)	0.0181 (5)	-0.0007 (3)	0.0053 (4)	-0.0001 (3)
N4	0.0153 (5)	0.0270 (5)	0.0176 (5)	-0.0005 (3)	0.0055 (4)	0.0017 (4)
O1	0.0192 (4)	0.0439 (5)	0.0244 (4)	-0.0026 (4)	0.0108 (3)	-0.0066 (4)
O2	0.0190 (4)	0.0441 (5)	0.0169 (4)	0.0043 (4)	0.0032 (3)	-0.0004 (3)
O3	0.0178 (4)	0.0344 (5)	0.0161 (4)	-0.0001 (3)	0.0062 (3)	0.0014 (3)
O4	0.0211 (4)	0.0510 (6)	0.0187 (4)	-0.0024 (4)	0.0056 (3)	-0.0028 (4)
O5	0.0204 (4)	0.0370 (5)	0.0172 (4)	0.0008 (3)	0.0071 (3)	0.0015 (3)
O6	0.0175 (4)	0.0853 (8)	0.0252 (5)	-0.0085 (5)	0.0069 (4)	-0.0130 (5)
O7	0.0190 (4)	0.0498 (6)	0.0193 (4)	-0.0038 (4)	0.0080 (3)	-0.0038 (4)
OW1	0.031 (3)	0.056 (3)	0.058 (3)	0.001 (2)	0.024 (2)	0.004 (2)

Geometric parameters (Å, °)

C1—N3	1.3223 (15)	C9—C10	1.3945 (16)
C1—C4	1.4557 (16)	C9—C13	1.5006 (16)
C1—C2	1.4708 (15)	C10—H10	0.9500
C2—O1	1.2140 (14)	C11—O4	1.2068 (14)
C2—N1	1.3864 (14)	C11—O5	1.3298 (14)
C3—O2	1.2242 (14)	C12—O5	1.4581 (14)
C3—N1	1.3638 (15)	C12—H12A	0.9800
C3—N2	1.3759 (15)	C12—H12B	0.9800
C4—O3	1.2387 (14)	C12—H12C	0.9800
C4—N2	1.3724 (14)	C13—O6	1.1944 (15)
C5—C6	1.3909 (16)	C13—O7	1.3280 (15)
C5—C10	1.3968 (16)	C14—O7	1.4533 (14)
C5—N4	1.4080 (14)	C14—H14A	0.9800
C6—C7	1.3936 (16)	C14—H14B	0.9800
C6—H6	0.9500	C14—H14C	0.9800
C7—C8	1.3926 (16)	N1—H1N	0.8580

C7—C11	1.4970 (15)	N2—H2N	0.8982
C8—C9	1.3963 (16)	N3—N4	1.2950 (14)
C8—H8	0.9500	N4—H4N	0.8557
N3—C1—C4	124.93 (10)	O4—C11—O5	124.04 (10)
N3—C1—C2	114.97 (10)	O4—C11—C7	123.45 (10)
C4—C1—C2	120.00 (10)	O5—C11—C7	112.50 (9)
O1—C2—N1	119.97 (10)	O5—C12—H12A	109.5
O1—C2—C1	125.19 (10)	O5—C12—H12B	109.5
N1—C2—C1	114.84 (9)	H12A—C12—H12B	109.5
O2—C3—N1	122.53 (10)	O5—C12—H12C	109.5
O2—C3—N2	121.04 (10)	H12A—C12—H12C	109.5
N1—C3—N2	116.41 (10)	H12B—C12—H12C	109.5
O3—C4—N2	120.22 (10)	O6—C13—O7	124.04 (11)
O3—C4—C1	123.21 (10)	O6—C13—C9	123.36 (11)
N2—C4—C1	116.56 (10)	O7—C13—C9	112.60 (9)
C6—C5—C10	121.20 (10)	O7—C14—H14A	109.5
C6—C5—N4	117.59 (10)	O7—C14—H14B	109.5
C10—C5—N4	121.20 (10)	H14A—C14—H14B	109.5
C5—C6—C7	119.25 (10)	O7—C14—H14C	109.5
C5—C6—H6	120.4	H14A—C14—H14C	109.5
C7—C6—H6	120.4	H14B—C14—H14C	109.5
C8—C7—C6	120.52 (10)	C3—N1—C2	126.63 (9)
C8—C7—C11	117.69 (10)	C3—N1—H1N	112.8
C6—C7—C11	121.79 (10)	C2—N1—H1N	120.6
C7—C8—C9	119.52 (10)	C4—N2—C3	125.51 (10)
C7—C8—H8	120.2	C4—N2—H2N	119.7
C9—C8—H8	120.2	C3—N2—H2N	114.8
C10—C9—C8	120.75 (11)	N4—N3—C1	120.55 (10)
C10—C9—C13	121.89 (10)	N3—N4—C5	120.38 (9)
C8—C9—C13	117.35 (10)	N3—N4—H4N	121.7
C9—C10—C5	118.75 (10)	C5—N4—H4N	117.9
C9—C10—H10	120.6	C11—O5—C12	115.04 (9)
C5—C10—H10	120.6	C13—O7—C14	115.50 (9)
N3—C1—C2—O1	-5.85 (17)	C6—C7—C11—O5	0.66 (15)
C4—C1—C2—O1	177.58 (11)	C10—C9—C13—O6	-170.65 (13)
N3—C1—C2—N1	174.41 (9)	C8—C9—C13—O6	9.75 (18)
C4—C1—C2—N1	-2.17 (15)	C10—C9—C13—O7	9.60 (16)
N3—C1—C4—O3	5.51 (18)	C8—C9—C13—O7	-170.00 (10)
C2—C1—C4—O3	-178.27 (10)	O2—C3—N1—C2	177.97 (11)
N3—C1—C4—N2	-173.94 (10)	N2—C3—N1—C2	-0.46 (17)
C2—C1—C4—N2	2.27 (15)	O1—C2—N1—C3	-178.47 (11)
C10—C5—C6—C7	-0.97 (16)	C1—C2—N1—C3	1.29 (17)
N4—C5—C6—C7	177.91 (10)	O3—C4—N2—C3	179.07 (11)
C5—C6—C7—C8	0.67 (16)	C1—C4—N2—C3	-1.46 (16)
C5—C6—C7—C11	-178.47 (10)	O2—C3—N2—C4	-177.92 (11)
C6—C7—C8—C9	0.14 (16)	N1—C3—N2—C4	0.53 (17)

C11—C7—C8—C9	179.32 (10)	C4—C1—N3—N4	-2.91 (17)
C7—C8—C9—C10	-0.68 (16)	C2—C1—N3—N4	-179.30 (9)
C7—C8—C9—C13	178.92 (10)	C1—N3—N4—C5	176.15 (10)
C8—C9—C10—C5	0.40 (16)	C6—C5—N4—N3	-179.84 (10)
C13—C9—C10—C5	-179.18 (10)	C10—C5—N4—N3	-0.97 (16)
C6—C5—C10—C9	0.43 (16)	O4—C11—O5—C12	0.65 (16)
N4—C5—C10—C9	-178.40 (10)	C7—C11—O5—C12	179.85 (9)
C8—C7—C11—O4	0.70 (17)	O6—C13—O7—C14	-1.96 (19)
C6—C7—C11—O4	179.87 (11)	C9—C13—O7—C14	177.79 (10)
C8—C7—C11—O5	-178.51 (10)		

Hydrogen-bond geometry (Å, °)

Cg2 is the centroid of the C5–C10 benzene ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1N \cdots O2 ⁱ	0.86	2.03	2.8800 (13)	174
N2—H2N \cdots O3 ⁱⁱ	0.90	2.01	2.8931 (15)	168
N4—H4N \cdots O3	0.86	2.02	2.6571 (15)	131
N4—H4N \cdots O1 ⁱⁱⁱ	0.86	2.59	2.9302 (14)	105
C6—H6 \cdots Ow1	0.95	2.14	3.061 (6)	163
C12—H12B \cdots O1 ^{iv}	0.98	2.39	3.2743 (17)	149
C14—H14B \cdots O4 ^v	0.98	2.53	3.4754 (16)	163
C12—H12C \cdots Cg2 ⁱⁱⁱ	0.98	2.73	3.4717 (15)	133

Symmetry codes: (i) $-x+1, y, -z+5/2$; (ii) $-x+1, y, -z+3/2$; (iii) $x, -y+1, z-1/2$; (iv) $x, y, z-1$; (v) $x, y, z+1$.