Synthesis, crystal structure and Hirshfeld surface analysis of 5-[2-(dicyanomethylidene)hydrazin-1-yl]-2,4,6-triiodoisophthalic acid ethanol monosolvate
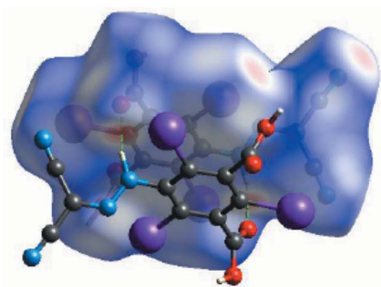
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The title compound, $C_{11}H_3I_3N_4O_4 \cdot C_2H_6O$, crystallizes in the triclinic $P\bar{1}$ space group with one independent molecule and one ethanol solvent molecule in the asymmetric unit. The benzene ring and the methylcarbonohydrazonoyl dicyanide group of the main molecule makes a dihedral angle of 57.91 (16)°. In the crystal, O—H···O and N—H···O hydrogen bonds link pairs of molecules, forming dimers with $R_2^2(14)$ motifs. These dimers are connected by O—H···O hydrogen bonds into chains along the a-axis direction, forming $R_2^2(16)$ ring motifs. Further O—H···O interactions involving the ethanol solvent molecule connect the chains into a three-dimensional network. In addition, C—I···π interactions are observed. The intermolecular interactions in the crystal structure were quantified and analysed using Hirshfeld surface analysis.

1. Chemical context

Arylhydrazones of active methylene compounds (AHAMC) have been extensively employed as ligands and precursors for the synthesis of coordination, organic or supramolecular compounds (Gurbanov et al., 2020a,b; Kopylovich et al., 2011). Besides their biological significance (Martins et al., 2017), the transition-metal complexes of AHAMC ligands have been found to possess a wide variety of functional properties, and have applications as catalysts, supramolecular building blocks and analytical reagents (Mahmudov et al., 2010, 2012, 2015). By the functionalization of the active methylene fragment (acetylacetone or barbituric acid) or the aromatic moiety (2,4,6-triiodoisophthalic acid) of the AHAMC molecules, the catalytic properties of their metal complexes can be improved in the nitroaldol reaction between aldehydes and nitroethane (Gurbanov et al., 2022). On the other hand, non-covalent interactions such as hydrogen, halogen and chalcogen bonds as well as π-interactions can be employed in the synthesis, catalysis and design of materials (Abdelhamid et al., 2011; Khalilov et al., 2021; Ma et al., 2021; Mahmudov et al., 2022). As well as hydrogen bonds, the cooperation of different weak bonds can act as a driving force for controlling supramolecular networks (Polyanskii et al., 2019; Safarova et al., 2019; Shikhaliyev et al., 2019; Zubkov et al., 2018). Similarly to Schiff base complexes (Mahmoudi et al., 2017a,b, 2019), the func-

tional groups can be involved in various types of inter-molecular interactions in metal complexes of arylhydrazone ligands. We have synthesized a new iodine-substituted AHAMC ligand, 5-[2-(dicyanomethylene)hydrazinyl]-2,4,6-triiodoisophthalic acid, and studied the intermolecular halogen bonds and other types of weak interactions in its crystal structure.
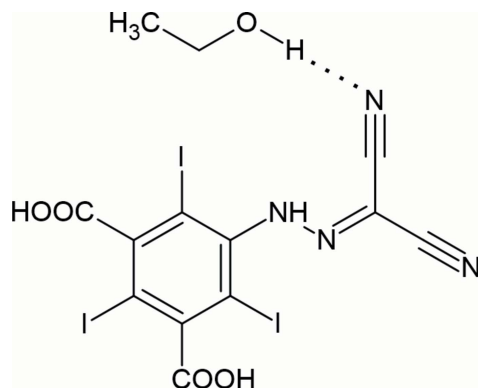
2. Structural commentary

The title compound (Fig. 1) crystallizes in the triclinic $P\bar{1}$ space group with one independent molecule and one ethanol solvent molecule in the asymmetric unit. The benzene ring (C1–C6) and the methylcarbonohydrazonoyl dicyanide group (N1–N4/C1/C7–C9) of the main molecule makes a dihedral angle of
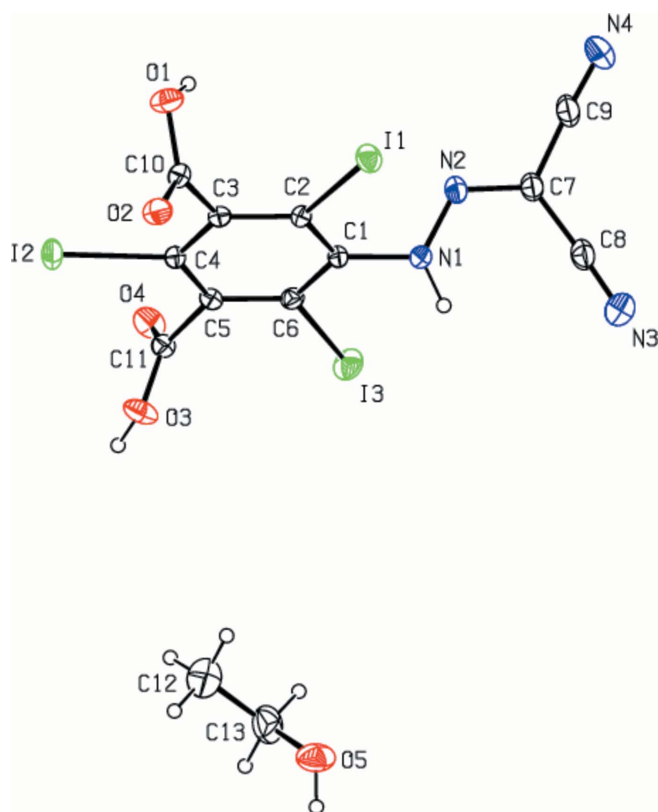

Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 30% probability level.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O4^i	0.85	1.80	2.648 (4)	178
O3—H3$\cdots$O5^{ii}	0.85	1.68	2.515 (4)	169
O5—H5$\cdots$N3^{iii}	0.85	2.40	3.200 (5)	156
N1—H1$N\cdots$O2^{iv}	0.92	2.11	2.937 (4)	149

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

57.91 (16)°. Geometric parameter values in the molecule are normal and in good agreement with the values in the compounds discussed in the *Database survey* section.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal of the title compound, pairs of molecules are linked by O—H$\cdots$O and N—H$\cdots$O hydrogen bonds, forming dimers with $R_2^2(14)$ motifs (Bernstein *et al.*, 1995; Table 1, Fig. 2). These dimers are connected along the *a*-axis direction by further O—H$\cdots$O hydrogen bonds, forming $R_2^2(16)$ ring motifs. O—H$\cdots$O hydrogen bonds involving the ethanol solvent molecule connect chains into a three-dimensional network. In addition, C—I$\cdots\pi$ interactions are also observed [C2—I1$\cdots Cg1(1 - x, 1 - y, 1 - z)$, 3.8441 (15) Å]. The carbon atoms in the arylhydrazone molecule are magnetically non-equivalent as a result of limited rotation around the C—N bond, thus the NH group is locked and becomes '*asymmetric*', which translates into diastereotopic protons and carbons in the title compound.

In order to present the intermolecular interactions in the crystal structure of the title compound in a visual manner, Hirshfeld surfaces and their associated two-dimensional fingerprint plots were generated using *CrystalExplorer17.5* (Spackman *et al.*, 2021). The Hirshfeld surface plotted over d_{norm} is shown in Fig. 3, while Fig. 4 shows the full two-dimensional fingerprint plot and those delineated into the
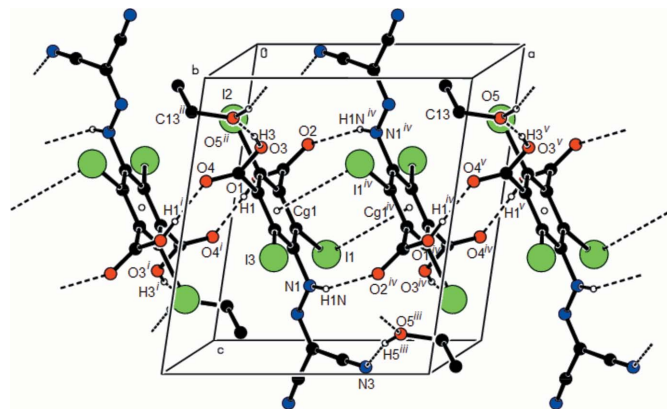

Figure 2
A part view of the molecular packing in the unit cell. N—H$\cdots$O, O—H$\cdots$O hydrogen bonds and C—I$\cdots\pi$ interactions are shown as dashed lines. Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x - 1, y, z$; (iii) $-x + 2, -y + 2, -z + 1$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x + 1, y, z$.
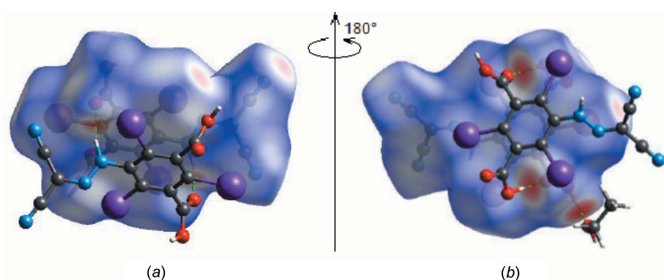
Figure 3
(*a*) Front and (*b*) back sides of the three-dimensional Hirshfeld surface of the title compound mapped over d_{norm}, with a fixed colour scale of −0.8291 to 1.0734 a.u.

major contacts: O···H/H···O (23.2%), N···H/H···N (11.9%), I···N/N···I (11.9%) and I···H/H···I (10.7%). Smaller contributions are made by I···C/C···I (7.7%), C···H/

H···C (6.7%), I···O/O···I (6.7%), I···I (5.4%), C···C (4.8%), H···H (2.3%), O···C/C···O(2.3%), N···C/C···N (2.1%), O···N/N···O (2.0%), O···O (1.4%) and N···N (1.0%) interactions.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.43, update June 2022; Groom *et al.*, 2016) for the *5-amino-2,4,6-triiodobenzene-1,3-dicarboxylic acid* unit gave four similar structures, *viz.* 5-amino-2,4,6-triiodoisophthalic acid monohydrate (SOGGUR; Beck & Sheldrick, 2008), 4-(4-pyridyl)pyridinium 3-amino-5-carboxy-2,4,6-triiodobenzoate–5-amino-2,4,6-triiodoisophthalic acid (1/1) (WADPAU; Zhang *et al.*, 2010), 5-amino-2,4,6-triiodoisophthalic acid–4,4′-bipyridine *N,N′*-dioxide–water (1/1/1) (UNUDIR; Zhang *et al.*, 2011) and 5-amino-2,4,6-tribromoisophthalic acid (BOTVUC; Beck *et al.*, 2009).

In the crystal structure of SOGGUR, molecules are linked by O—H···O, N—H···O and O—H···N hydrogen bonds involving all possible donors and also the water molecule, forming an extensive hydrogen-bond network.

In the ammonium carboxylate–carboxylic acid co-crystal WADPAU, the carboxylate anion and carboxylic acid molecule are linked by O—H···O and N—H···O hydrogen bonds, forming a chain running along the *c*-axis direction of the monoclinic unit cell. The chains are linked by pyridinium and pyridine N—H···O hydrogen bonds, generating a layer motif. O—H···N and O—H···O hydrogen bonds are also observed.

In the crystal of UNUDIR, molecules are linked by O—H···O hydrogen bonds into a three-dimensional network. An N—H···O interaction also occurs. One of the amino H atoms is not involved in hydrogen bonding.

In the crystal structure of BOTVUC, molecules are linked into chains by COO—H···O bonds, and pairs of chains are connected by additional COO—H···O interactions. This chain bundle shows stacking interactions and weak N—H···O hydrogen bonds with adjacent chains.

5. Synthesis and crystallization

Diazotization: 558 mg (1 mmol) of 5-amino-2,4,6-triiodo-isophthalic acid were dissolved in 15 mL of water, and the solution was cooled in an ice bath to 273 K, then 69 mg (1 mmol) of NaNO₂ were added followed by 0.2 mL of HCl, and mixed for 1 h. The temperature of the mixture should not exceed 278 K.

Azocoupling: NaOH (40 mg, 1 mmol) was added to a mixture of 1 mmol (66 mg) of malononitrile with 5 mL of water. The solution was cooled in 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 precipitate was filtered off, recrystallized from methanol and dried in air. Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution.

Figure 4
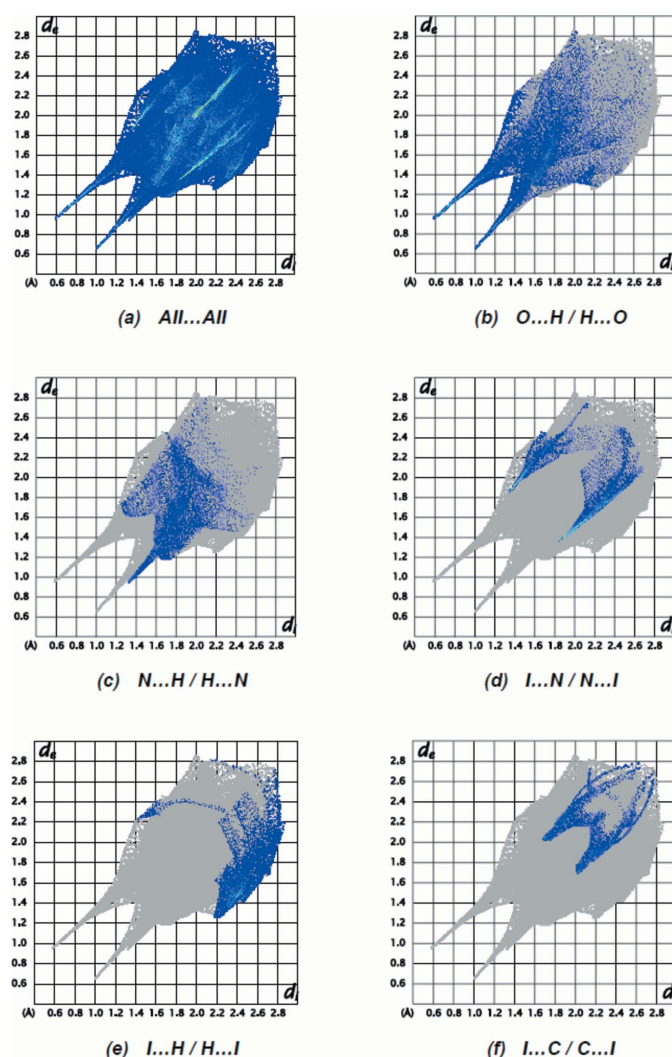The two-dimensional fingerprint plots of the title compound, showing (*a*) all interactions, and delineated into (*b*) O···H/H···O, (*c*) N···H/H···N, (*d*) I···N/N···I, (*e*) I···H/H···I and (*f*) I···C/C···I interactions. [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively.]

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_3I_3N_4O_4 \cdot C_2H_6O$
M_r	681.94
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	296
a, b, c (Å)	9.1499 (3), 9.8771 (3), 12.0440 (4)
α, β, γ (°)	113.512 (1), 95.399 (1), 103.462 (1)
V (Å^3)	949.11 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.97
Crystal size (mm)	$0.26 \times 0.21 \times 0.14$
Data collection	
Diffractometer	Bruker D8 Quest PHOTON 100 detector
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.325, 0.518
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	20253, 3755, 3375
R_{int}	0.025
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.054, 1.22
No. of reflections	3755
No. of parameters	227
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.75, −0.61

Computer programs: *APEX4* and *SAINT* (Bruker, 2008), *SHELXT2019/1* (Sheldrick, 2015a), *SHELXL2019/1* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

The title compound: Yield 79% (based on malononitrile), yellow powder soluble in DMSO, methanol, ethanol and DMF. Analysis calculated for $C_{13}H_9I_3N_4O_5$: C 22.90, H 1.33, N 8.22; found: C 22.87, H 1.30, N 8.18 %. ESI–MS: *m/z*: 636.88. IR (KBr): 3123 ν(NH), 2937 ν(NH), 2233 ν(CN) and 1707 ν(C=N) cm^{-1}. ^{1}H NMR (300.130 MHz, DMSO-d_6, internal TMS): δ 1.02–1.06 (3H, CH$_3$), 3.42–3.47 (2H, CH$_2$), 7.25 and 7.32 (2H, COOH) and 11.21 (1H, N—H). ^{1}H, in ^{13}C{^{1}H} NMR (75.468 MHz, DMSO-d_6): δ 18.56 (CH$_3$), 56.78 (CH$_2$), 85.37, 89.06 and 94.93 (3C–I), 96.80 (C=N), 109.71 and 109.91 (CN), 149.79 and 150.13 (CCOOH), 162.97 (C–NH), 169.48 and 169.79 (C=O).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atoms of the ethanol molecule were placed at idealized positions and refined using a riding model, with U_{iso}(H) values assigned as $1.2U_{eq}$ or $1.5U_{eq}$(methyl only) of the parent atoms, with C—H distances of 0.97 (methylene) and 0.96 Å (methyl). The remaining hydrogen atoms bound to nitrogen and oxygen were located in difference-Fourier maps and refined with fixed positional thermal displacement parameters and with U_{iso}(H) values assigned as $1.2U_{eq}$(NH) or $1.5U_{eq}$(OH) of the parent atoms. One reflection, (001), affected by the incident beam-stop was omitted in the final cycles of refinement.

References

Abdelhamid, A. A., Mohamed, S. K., Khalilov, A. N., Gurbanov, A. V. & Ng, S. W. (2011). *Acta Cryst.* E**67**, o744.

Beck, T., Herbst-Irmer, R. & Sheldrick, G. M. (2009). *Acta Cryst.* C**65**, o237–o239.

Beck, T. & Sheldrick, G. M. (2008). *Acta Cryst.* E**64**, o1286.

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

Bruker (2008). *APEX4* 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., Karmakar, A., Aliyeva, V. A., Mahmudov, K. T. & Pombeiro, A. J. L. (2022). *Dalton Trans.* **51**, 1019–1031.

Gurbanov, A. V., Kuznetsov, M. L., Mahmudov, K. T., Pombeiro, A. J. L. & Resnati, G. (2020b). *Chem. Eur. J.* **26**, 14833–14837.

Khalilov, A. N., Tüzün, B., Taslimi, P., Tas, A., Tuncbilek, Z. & Cakmak, N. K. (2021). *J. Mol. Liq.* **344**, 117761.

Kopylovich, M. N., Mahmudov, K. T., Guedes da Silva, M. F. C., Martins, L. M. D. R. S., Kuznetsov, M. L., Silva, T. F. S., Fraústo da Silva, J. J. R. & Pombeiro, A. J. L. (2011). *J. Phys. Org. Chem.* **24**, 764–773.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

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.

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., 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., Zaręba, J. K., Gurbanov, A. V., Bauzá, A., Zubkov, F. I., Kubicki, M., Stilinović, V., Kinzhybalo, V. & Frontera, A. (2017b). *Eur. J. Inorg. Chem.* pp. 4763–4772.

Mahmudov, K. T., Guedes da Silva, M. F. C., Glucini, M., Renzi, M., Gabriel, K. C. P., Kopylovich, M. N., Sutradhar, M., Marchetti, F., Pettinari, C., Zamponi, S. & Pombeiro, A. J. L. (2012). *Inorg. Chem. Commun.* **22**, 187–189.

Mahmudov, K. T., Gurbanov, A. V., Aliyeva, V. A., Guedes da Silva, M. F. C., Resnati, G. & Pombeiro, A. J. L. (2022). *Coord. Chem. Rev.* **464**, 214556.

Mahmudov, K. T., Maharramov, A. M., Aliyeva, R. A., Aliyev, I. A., Kopylovich, M. N. & Pombeiro, A. J. L. (2010). *Anal. Lett.* **43**, 2923–2938.

Mahmudov, K. T., Sutradhar, M., Martins, L. M. D. R. S., Guedes da Silva, F. C., Ribera, A., Nunes, A. V. M., Gahramanova, S. I.,

Marchetti, F. & Pombeiro, A. J. L. (2015). *RSC Adv.* **5**, 25979–25987.

Martins, N. M. R., Anbu, S., Mahmudov, K. T., Ravishankaran, R., Guedes da Silva, M. F. C., Martins, L. M. D. R. S., Karande, A. A. & Pombeiro, A. J. L. (2017). *New J. Chem.* **41**, 4076–4086.

Polyanskii, K. B., Alekseeva, K. A., Raspertov, P. V., Kumandin, P. A., Nikitina, E. V., Gurbanov, A. V. & Zubkov, F. I. (2019). *Beilstein J. Org. Chem.* **15**, 769–779.

Safavora, A. S., Brito, I., Cisterna, J., Cárdenas, A., Huseynov, E. Z., Khalilov, A. N., Naghiyev, F. N., Askerov, R. K. & Maharramov, A. M. Z. (2019). *Z. Kristallogr. New Cryst. Struct.* **234**, 1183–1185.

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

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

Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.

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

Zhang, K.-L., Diao, G.-W. & Ng, S. W. (2010). *Acta Cryst.* E**66**, o3165.

Zhang, K.-L., Zhang, J.-B. & Ng, S. W. (2011). *Acta Cryst.* E**67**, o793.

Zubkov, F. I., Mertsalov, D. F., Zaytsev, V. P., Varlamov, A. V., Gurbanov, A. V., Dorovatovskii, P. V., Timofeeva, T. V., Khrustalev, V. N. & Mahmudov, K. T. (2018). *J. Mol. Liq.* **249**, 949–952.

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Fargana S. Aliyeva, Gunay Z. Mammadova, Mehmet Akkurt, Sevim Türktekin Çelikesir and Ajaya Bhattarai

Computing details

Data collection: *APEX4* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXT2019/1* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2019/1* (Sheldrick, 2015*b*); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

5-[2-(Dicyanomethylidene)hydrazin-1-yl]-2,4,6-triiodoisophthalic acid ethanol monosolvate

Crystal data

$C_{11}H_3I_3N_4O_4 \cdot C_2H_6O$	$Z = 2$
$M_r = 681.94$	$F(000) = 628$
Triclinic, $P\overline{1}$	$D_x = 2.386$ Mg m^{-3}
$a = 9.1499$ (3) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.8771$ (3) Å	Cell parameters from 9873 reflections
$c = 12.0440$ (4) Å	$\theta = 2.3–26.4°$
$\alpha = 113.512$ (1)°	$\mu = 4.97$ mm^{-1}
$\beta = 95.399$ (1)°	$T = 296$ K
$\gamma = 103.462$ (1)°	Prism, orange
$V = 949.11$ (5) Å^3	$0.26 \times 0.21 \times 0.14$ mm

Data collection

Bruker D8 Quest PHOTON 100 detector diffractometer	3755 independent reflections
φ and ω scans	3375 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$R_{int} = 0.025$
	$\theta_{max} = 26.4°$, $\theta_{min} = 2.3°$
	$h = -11 \rightarrow 11$
$T_{min} = 0.325$, $T_{max} = 0.518$	$k = -12 \rightarrow 12$
20253 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.024$	
$wR(F^2) = 0.054$	
$S = 1.22$	Hydrogen site location: mixed
3755 reflections	H-atom parameters constrained
227 parameters	$w = 1/[\sigma^2(F_o^2) + 2.2238P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.75$ e Å^{-3}

$\Delta\rho_{min} = -0.61$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.43837 (3)	0.36375 (3)	0.66860 (2)	0.03614 (8)
I2	0.00185 (3)	0.27921 (3)	0.22009 (2)	0.03995 (8)
I3	0.34230 (3)	0.92158 (3)	0.61552 (3)	0.04489 (9)
O1	0.0961 (3)	0.1098 (3)	0.4380 (3)	0.0419 (6)
H1	0.063676	0.171314	0.495416	0.063*
O2	0.2676 (3)	0.1256 (3)	0.3246 (2)	0.0380 (6)
O3	0.1880 (3)	0.6581 (4)	0.2734 (3)	0.0433 (7)
H3	0.165558	0.704626	0.231145	0.065*
O4	0.0089 (3)	0.7033 (4)	0.3831 (3)	0.0438 (7)
O5	1.0910 (4)	0.7945 (4)	0.1586 (3)	0.0600 (9)
H5	1.151655	0.834890	0.123379	0.090*
N1	0.4566 (3)	0.7189 (3)	0.7341 (3)	0.0315 (6)
H1N	0.532784	0.799315	0.735139	0.038*
N2	0.4222 (3)	0.7013 (4)	0.8311 (3)	0.0326 (6)
N3	0.7600 (5)	1.0028 (5)	0.9762 (4)	0.0656 (12)
N4	0.4455 (6)	0.7440 (5)	1.1278 (4)	0.0656 (12)
C1	0.3561 (4)	0.6188 (4)	0.6179 (3)	0.0260 (7)
C2	0.3273 (3)	0.4583 (4)	0.5705 (3)	0.0249 (6)
C3	0.2269 (4)	0.3621 (4)	0.4560 (3)	0.0262 (7)
C4	0.1576 (4)	0.4260 (4)	0.3895 (3)	0.0258 (7)
C5	0.1879 (4)	0.5859 (4)	0.4348 (3)	0.0267 (7)
C6	0.2875 (4)	0.6808 (4)	0.5487 (3)	0.0262 (7)
C7	0.5133 (4)	0.7872 (4)	0.9390 (3)	0.0348 (8)
C8	0.6530 (5)	0.9076 (5)	0.9622 (3)	0.0398 (9)
C9	0.4713 (5)	0.7606 (5)	1.0428 (4)	0.0437 (9)
C10	0.1991 (4)	0.1893 (4)	0.4015 (3)	0.0296 (7)
C11	0.1178 (4)	0.6559 (4)	0.3606 (3)	0.0294 (7)
C12	0.8376 (7)	0.6247 (7)	0.0688 (6)	0.0785 (17)
H12A	0.731327	0.619981	0.052211	0.118*
H12B	0.850672	0.568988	0.116680	0.118*
H12C	0.869243	0.579198	−0.008073	0.118*
C13	0.9323 (6)	0.7882 (7)	0.1389 (5)	0.0646 (14)
H13A	0.915521	0.846280	0.092754	0.078*
H13B	0.903196	0.833807	0.217868	0.078*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.04006 (14)	0.03692 (13)	0.03368 (13)	0.01326 (10)	0.00214 (10)	0.01774 (10)
I2	0.03979 (14)	0.03778 (14)	0.02815 (13)	0.00210 (10)	−0.00658 (10)	0.00856 (10)
I3	0.05157 (16)	0.02331 (12)	0.05002 (16)	0.00527 (10)	0.00314 (12)	0.01113 (11)
O1	0.0475 (16)	0.0294 (13)	0.0477 (16)	0.0067 (12)	0.0229 (13)	0.0155 (12)
O2	0.0432 (15)	0.0294 (13)	0.0371 (14)	0.0089 (11)	0.0160 (12)	0.0095 (11)
O3	0.0468 (16)	0.0641 (18)	0.0457 (16)	0.0286 (14)	0.0219 (13)	0.0408 (15)
O4	0.0432 (15)	0.0589 (18)	0.0422 (15)	0.0288 (14)	0.0164 (12)	0.0255 (14)
O5	0.0564 (19)	0.069 (2)	0.081 (2)	0.0197 (17)	0.0171 (17)	0.057 (2)
N1	0.0339 (15)	0.0276 (14)	0.0257 (14)	−0.0020 (12)	0.0005 (12)	0.0119 (12)
N2	0.0340 (16)	0.0339 (16)	0.0241 (14)	0.0074 (13)	0.0016 (12)	0.0092 (12)
N3	0.062 (3)	0.061 (3)	0.054 (2)	−0.010 (2)	−0.002 (2)	0.023 (2)
N4	0.082 (3)	0.072 (3)	0.033 (2)	0.004 (2)	0.0039 (19)	0.024 (2)
C1	0.0239 (15)	0.0290 (16)	0.0196 (15)	0.0023 (13)	0.0028 (12)	0.0087 (13)
C2	0.0204 (15)	0.0278 (16)	0.0241 (15)	0.0027 (12)	0.0015 (12)	0.0120 (13)
C3	0.0233 (15)	0.0291 (16)	0.0259 (16)	0.0038 (13)	0.0060 (13)	0.0137 (14)
C4	0.0261 (16)	0.0253 (16)	0.0209 (15)	0.0028 (13)	0.0038 (12)	0.0079 (13)
C5	0.0283 (16)	0.0293 (16)	0.0229 (15)	0.0068 (13)	0.0076 (13)	0.0122 (13)
C6	0.0281 (16)	0.0217 (15)	0.0269 (16)	0.0042 (13)	0.0066 (13)	0.0102 (13)
C7	0.0380 (19)	0.0336 (18)	0.0267 (17)	0.0075 (15)	0.0001 (15)	0.0102 (15)
C8	0.048 (2)	0.035 (2)	0.0275 (18)	0.0093 (18)	−0.0007 (16)	0.0084 (16)
C9	0.049 (2)	0.044 (2)	0.0283 (19)	0.0081 (18)	−0.0034 (17)	0.0112 (17)
C10	0.0291 (17)	0.0253 (16)	0.0278 (17)	0.0029 (14)	0.0030 (14)	0.0087 (14)
C11	0.0313 (17)	0.0289 (17)	0.0262 (16)	0.0062 (14)	0.0065 (14)	0.0116 (14)
C12	0.073 (4)	0.077 (4)	0.068 (4)	0.007 (3)	0.005 (3)	0.024 (3)
C13	0.063 (3)	0.072 (3)	0.058 (3)	0.016 (3)	−0.009 (2)	0.034 (3)

Geometric parameters (Å, º)

I1—C2	2.097 (3)	C1—C6	1.397 (5)
I2—C4	2.104 (3)	C1—C2	1.401 (5)
I3—C6	2.097 (3)	C2—C3	1.399 (4)
O1—C10	1.307 (4)	C3—C4	1.392 (5)
O1—H1	0.8499	C3—C10	1.511 (5)
O2—C10	1.214 (4)	C4—C5	1.396 (5)
O3—C11	1.287 (4)	C5—C6	1.390 (5)
O3—H3	0.8500	C5—C11	1.510 (5)
O4—C11	1.205 (4)	C7—C8	1.444 (6)
O5—C13	1.432 (6)	C7—C9	1.445 (6)
O5—H5	0.8500	C12—C13	1.481 (8)
N1—N2	1.303 (4)	C12—H12A	0.9600
N1—C1	1.419 (4)	C12—H12B	0.9600
N1—H1N	0.9222	C12—H12C	0.9600
N2—C7	1.300 (5)	C13—H13A	0.9700
N3—C8	1.134 (6)	C13—H13B	0.9700
N4—C9	1.136 (6)		

C10—O1—H1	109.4	C1—C6—I3	119.1 (2)
C11—O3—H3	120.3	N2—C7—C8	124.6 (3)
C13—O5—H5	119.8	N2—C7—C9	117.6 (3)
N2—N1—C1	117.7 (3)	C8—C7—C9	117.8 (3)
N2—N1—H1N	125.8	N3—C8—C7	177.0 (4)
C1—N1—H1N	115.9	N4—C9—C7	176.6 (5)
C7—N2—N1	119.9 (3)	O2—C10—O1	120.9 (3)
C6—C1—C2	119.5 (3)	O2—C10—C3	121.4 (3)
C6—C1—N1	119.8 (3)	O1—C10—C3	117.6 (3)
C2—C1—N1	120.7 (3)	O4—C11—O3	125.5 (3)
C3—C2—C1	119.5 (3)	O4—C11—C5	122.5 (3)
C3—C2—I1	120.3 (2)	O3—C11—C5	112.0 (3)
C1—C2—I1	120.1 (2)	C13—C12—H12A	109.5
C4—C3—C2	120.0 (3)	C13—C12—H12B	109.5
C4—C3—C10	119.7 (3)	H12A—C12—H12B	109.5
C2—C3—C10	120.2 (3)	C13—C12—H12C	109.5
C3—C4—C5	120.9 (3)	H12A—C12—H12C	109.5
C3—C4—I2	119.4 (2)	H12B—C12—H12C	109.5
C5—C4—I2	119.7 (2)	O5—C13—C12	109.1 (5)
C6—C5—C4	118.8 (3)	O5—C13—H13A	109.9
C6—C5—C11	120.1 (3)	C12—C13—H13A	109.9
C4—C5—C11	121.0 (3)	O5—C13—H13B	109.9
C5—C6—C1	121.2 (3)	C12—C13—H13B	109.9
C5—C6—I3	119.6 (2)	H13A—C13—H13B	108.3
C1—N1—N2—C7	177.9 (3)	C4—C5—C6—C1	−0.3 (5)
N2—N1—C1—C6	121.9 (3)	C11—C5—C6—C1	−178.8 (3)
N2—N1—C1—C2	−59.3 (4)	C4—C5—C6—I3	177.5 (2)
C6—C1—C2—C3	−1.7 (5)	C11—C5—C6—I3	−1.0 (4)
N1—C1—C2—C3	179.5 (3)	C2—C1—C6—C5	1.6 (5)
C6—C1—C2—I1	176.7 (2)	N1—C1—C6—C5	−179.7 (3)
N1—C1—C2—I1	−2.0 (4)	C2—C1—C6—I3	−176.2 (2)
C1—C2—C3—C4	0.6 (5)	N1—C1—C6—I3	2.5 (4)
I1—C2—C3—C4	−177.8 (2)	N1—N2—C7—C8	1.6 (6)
C1—C2—C3—C10	177.7 (3)	N1—N2—C7—C9	−178.7 (3)
I1—C2—C3—C10	−0.7 (4)	C4—C3—C10—O2	79.7 (4)
C2—C3—C4—C5	0.6 (5)	C2—C3—C10—O2	−97.4 (4)
C10—C3—C4—C5	−176.5 (3)	C4—C3—C10—O1	−98.9 (4)
C2—C3—C4—I2	−178.2 (2)	C2—C3—C10—O1	84.0 (4)
C10—C3—C4—I2	4.7 (4)	C6—C5—C11—O4	−79.6 (5)
C3—C4—C5—C6	−0.8 (5)	C4—C5—C11—O4	102.0 (4)
I2—C4—C5—C6	178.0 (2)	C6—C5—C11—O3	100.3 (4)
C3—C4—C5—C11	177.6 (3)	C4—C5—C11—O3	−78.1 (4)
I2—C4—C5—C11	−3.6 (4)		

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O4[i]	0.85	1.80	2.648 (4)	178
O3—H3⋯O5[ii]	0.85	1.68	2.515 (4)	169
O5—H5⋯N3[iii]	0.85	2.40	3.200 (5)	156
N1—H1N⋯O2[iv]	0.92	2.11	2.937 (4)	149

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