



Crystal structure and Hirshfeld surface analysis of 2,5-dibromoterephthalic acid ethylene glycol monosolvate

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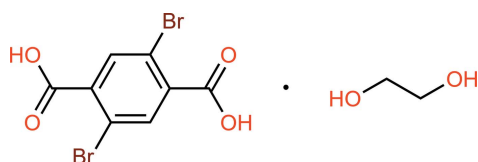
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The title compound, $C_8H_4Br_2O_4 \cdot C_2H_6O_2$, crystallizes with one-half of a 2,5-dibromoterephthalic acid (H_2Br_2tp) molecule and one-half of an ethylene glycol (EG) molecule in the the asymmetric unit. The whole molecules are generated by application of inversion symmetry. The H_2Br_2tp molecule is not planar, with the dibromobenzene ring system inclined by a dihedral angle of $18.62(3)^\circ$ to the carboxylic group. In the crystal, the H_2Br_2tp and EG molecules are linked into sheets propagating parallel to $(\bar{1}01)$ through $O-H \cdots O$ hydrogen bonds, thereby forming $R_4^4(12)$ and $R_4^4(28)$ graph-set motifs. $Br \cdots O$ and weak $\pi-\pi$ stacking interactions are also observed. Hirshfeld surface analysis was used to confirm the existence of these interactions.

1. Chemical context

Terephthalic acid and its derivatives are important ligands in the construction of coordination frameworks with high dimensionalities and interesting topologies (Li *et al.*, 1999; Seidel *et al.*, 2011). They have also been shown to be versatile building blocks in crystal engineering to drive the self-assembly of functional supramolecular networks through intermolecular interactions such as hydrogen bonds, halogen bonds, and aromatic $\pi-\pi$ stacking interactions (Lemmerer, 2011; Karmakar *et al.*, 2014; Meng *et al.*, 2015).



In this study, we present the crystal structure of 2,5-dibromoterephthalic acid ethylene glycol monosolvate, $C_8H_4Br_2O_4 \cdot C_2H_6O_2$ or $H_2Br_2tp \cdot EG$, which is a pseudopolymorph of the previously reported compound 2,5-dibromoterephthalic acid dihydrate (Song *et al.*, 2008).

2. Structural commentary

The structures of the molecular components in the title compound are shown in Fig. 1. The asymmetric unit contains one-half of a H_2Br_2tp molecule and one-half of an EG molecule. Both molecules are generated by application of inversion symmetry. The H_2Br_2tp molecule is not planar. Its

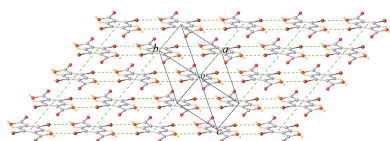


Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 \cdots O3	0.83 (1)	1.75 (1)	2.559 (3)	165 (4)
O3–H3 \cdots O2 ⁱ	0.82 (1)	1.97 (1)	2.767 (3)	166 (4)

Symmetry code: (i) $-x + 2, -y + 1, -z + 2$.

dibromobenzene ring system (r.m.s. deviation = 0.006 Å) makes a dihedral angle of 18.62 (3)° with the carboxylic group (r.m.s. deviation = 0.013 Å). As a result of symmetry restrictions, the EG molecule adopts an *anti*-conformation with an O3–C5–C5ⁱ–O3ⁱ torsion angle of 180° [symmetry code: (i) $2 - x, -y, 2 - z$].

3. Supramolecular features

In the crystal, the H₂Br₂tp and EG molecules are linked by strong-to-medium O–H \cdots O hydrogen bonds between carboxylic acid and alcohol OH functions (Table 1), enclosing R_4^4 (12) and R_4^4 (28) graph-set motifs and forming sheets parallel to the ($\bar{1}01$) plane; Fig. 2. Br \cdots O halogen bonding [Br \cdots O = 3.2536 (4) Å; C–Br \cdots O = 157.7 (3)°] and weak π – π stacking interactions [centroid-to-centroid distance = 4.283 (5) Å] are also observed (Fig. 3). The combination of these intermolecular interactions results in the formation of a three-dimensional supramolecular network.

4. Hirshfeld surface analysis

Hirshfeld surfaces (McKinnon *et al.*, 2007) and their associated two-dimensional fingerprint plots (Spackman & McKinnon, 2002) were used to quantify the various intermolecular interactions, and were generated using *Crystal-Explorer17* (Turner *et al.*, 2017). The shorter and longer contacts are indicated as red and blue spots on the Hirshfeld surfaces, and contacts with distances equal to the sum of the van der Waals radii are represented as white spots. Hirshfeld surfaces of the title compound mapped over the normalized distance, d_{norm} , using a standard surface resolution with a fixed

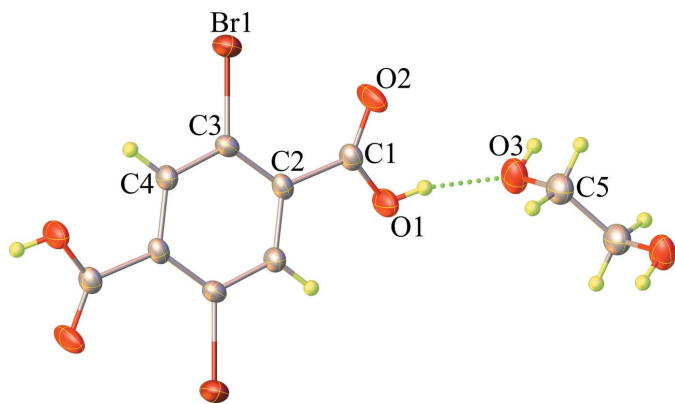


Figure 1
The structures of the molecular components in the title compound with displacement ellipsoids drawn at the 50% probability level. The O–H \cdots O hydrogen bond is shown by a dashed line.

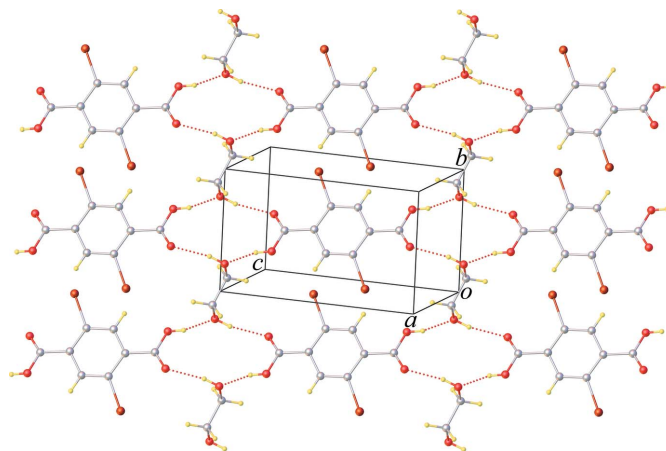


Figure 2
View of a supramolecular two-dimensional sheet parallel to the ($\bar{1}01$) direction, enclosing R_4^4 (12) and R_4^4 (28) graph-set motifs, sustained by O–H \cdots O hydrogen bonds (dashed lines).

colour scale of -0.7877 (red) to 0.9385 a.u. (blue) and the two-dimensional fingerprint plots are illustrated in Fig. 4. The dominant interactions between H and O atoms, corresponding to the discussed O–H \cdots O hydrogen bonds, can be clearly be seen as red spots on the Hirshfeld surface. The faint-red spot visible on the d_{norm} surface can be assigned to Br \cdots O contacts. Analysis of the two-dimensional fingerprint plots reveals that the H \cdots O/O \cdots H (28.8%) contacts are the dominant contributors to the Hirshfeld surface. The contribution of the Br \cdots H/H \cdots Br contacts is 22.1%, whereas Br \cdots Br contacts are negligible (0.9%). Other contacts *viz.* H \cdots H (17.7%), H \cdots C/C \cdots H (7.7%), Br \cdots C/C \cdots Br (7.2%), Br \cdots O/O \cdots Br (5.8%), C \cdots O/O \cdots C (4.5%), C \cdots C (3.3%) and O \cdots O (2.2%) also make significant contributions to the Hirshfeld surface.

5. Database survey

A search of the Cambridge Structural Database (Version 5.40, latest update May 2019; Groom *et al.*, 2016) for the H₂Br₂tp entity resulted in just two matches. In the structure of the pseudopolymorphic H₂Br₂tp dihydrate (CSD refcode POFROS; Song *et al.*, 2008), the H₂Br₂tp molecules are connected through water molecules by O–H \cdots O hydrogen bonds, forming a three-dimensional supramolecular network.

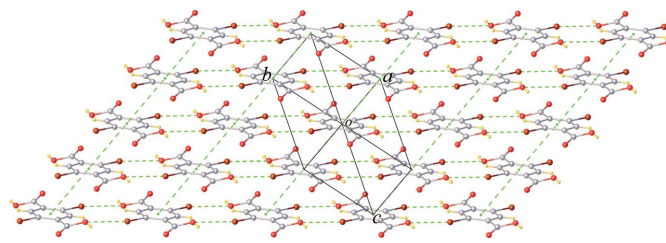
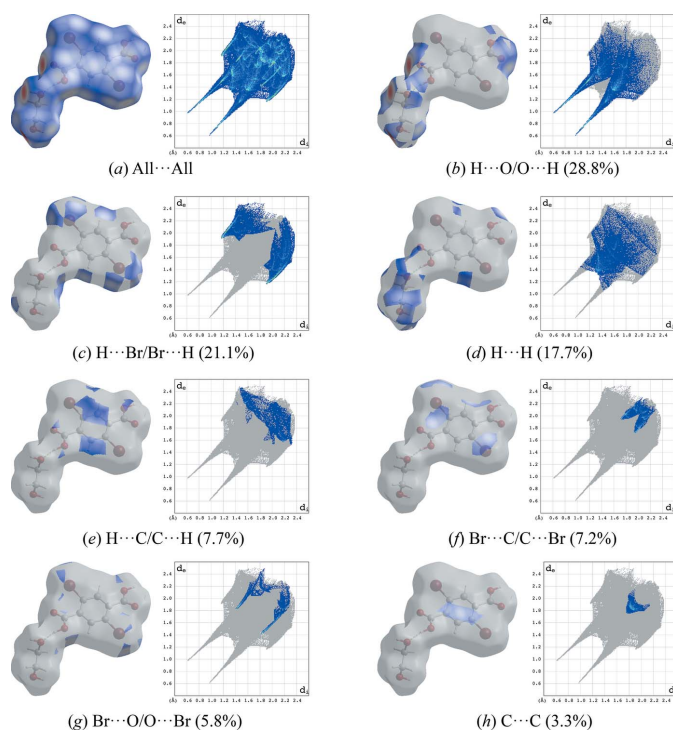


Figure 3
View along [111] of a supramolecular sheet sustained by Br \cdots O halogen bonding and π – π stacking interactions (dashed lines).


Figure 4

Two-dimensional fingerprint plots of the title compound, showing (a) all interactions, and delineated into (b) H...O/O...H, (c) H...Br/Br...H, (d) H...H, (e) H...C/C...H, (f) Br...C/C...Br, (g) Br...O/O...Br, and (h) C...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].

In the structure of bis[*N*-[1-(pyridin-2-yl- κ *N*)ethylidene]pyridine-4-carbohydrazonato- κ^2 *N',O*]nickel(II)-2,5-dibromoterephthalic acid (OBOJEX; Nakanishi & Sato, 2017), the H₂Br₂tp molecules form hydrogen-bonded zigzag chains with the complex molecules. The packing is further consolidated by π - π stacking and Br...Br halogen bonding.

6. Synthesis and crystallization

H₂Br₂tp and EG were purchased from commercial sources and used as received. A solution of H₂Br₂tp (0.020 g) in 5 ml of EG was heated (333 K) to reflux for 15 min. The reaction solution was held for 2–3 h and colourless block-shaped crystals suitable for single-crystal X-ray diffraction analysis were obtained.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The carbon-bound H atoms were placed in geometrically calculated positions and refined as riding with C–H = 0.93 Å for aromatic and C–H = 0.97 Å for methylene hydrogen atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms bound to O atoms were located from difference-Fourier maps but were refined with distance restraints of O–H = 0.82 ± 0.02 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₈ H ₄ Br ₂ O ₄ ·C ₂ H ₆ O ₂
M_r	386.00
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	296
a, b, c (Å)	4.2823 (6), 6.2607 (9), 11.5497 (17)
α, β, γ (°)	96.701 (5), 93.930 (5), 90.575 (5)
V (Å ³)	306.76 (8)
Z	1
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	6.62
Crystal size (mm)	0.20 × 0.20 × 0.16
Data collection	
Diffractometer	Bruker D8 QUEST CMOS PHOTON II
Absorption correction	Multi-scan (SADABS; Bruker, 2016)
$T_{\text{min}}, T_{\text{max}}$	0.576, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9075, 1208, 1076
R_{int}	0.052
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.023, 0.052, 1.05
No. of reflections	1208
No. of parameters	91
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.34, -0.28

Computer programs: APEX3 and SAINT (Bruker, 2016), SHELXT (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b and OLEX2 (Dolomanov et al., 2009).

Acknowledgements

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

(I)

Crystal data

$C_8H_4Br_2O_4 \cdot C_2H_6O_2$

$M_r = 386.00$

Triclinic, $P\bar{1}$

$a = 4.2823$ (6) Å

$b = 6.2607$ (9) Å

$c = 11.5497$ (17) Å

$\alpha = 96.701$ (5)°

$\beta = 93.930$ (5)°

$\gamma = 90.575$ (5)°

$V = 306.76$ (8) Å³

$Z = 1$

$F(000) = 188$

$D_x = 2.089$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5153 reflections

$\theta = 3.3$ – 28.8 °

$\mu = 6.62$ mm⁻¹

$T = 296$ K

Block, light colourless

$0.20 \times 0.20 \times 0.16$ mm

Data collection

Bruker D8 QUEST CMOS PHOTON II diffractometer

Radiation source: sealed x-ray tube, Micro focus tube

Graphite monochromator

Detector resolution: 7.39 pixels mm⁻¹

ω and φ scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2016)

$T_{\min} = 0.576$, $T_{\max} = 0.747$

9075 measured reflections

1208 independent reflections

1076 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 3.3$ °

$h = -5 \rightarrow 5$

$k = -7 \rightarrow 7$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.052$

$S = 1.05$

1208 reflections

91 parameters

2 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0175P)^2 + 0.2228P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL-2018/3

(Sheldrick 2018),

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.034 (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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.28840 (7)	0.90781 (4)	0.67985 (2)	0.03714 (15)
O1	0.9576 (5)	0.3651 (3)	0.75182 (16)	0.0399 (5)
H1	1.013 (9)	0.352 (6)	0.8205 (14)	0.071 (12)*
O2	0.6124 (5)	0.5932 (3)	0.82669 (15)	0.0430 (5)
O3	1.1223 (5)	0.2556 (3)	0.95346 (17)	0.0415 (5)
H3	1.205 (8)	0.320 (5)	1.0136 (19)	0.065 (12)*
C1	0.7228 (6)	0.4945 (4)	0.7436 (2)	0.0263 (5)
C2	0.6046 (5)	0.5048 (4)	0.6187 (2)	0.0231 (5)
C3	0.4170 (6)	0.6668 (4)	0.5809 (2)	0.0244 (5)
C4	0.3155 (6)	0.6610 (4)	0.4647 (2)	0.0261 (5)
H4	0.190106	0.770860	0.441344	0.031*
C5	0.9128 (7)	0.0972 (4)	0.9857 (2)	0.0371 (6)
H5A	0.756819	0.056821	0.921709	0.044*
H5B	0.805174	0.156980	1.052949	0.044*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0530 (2)	0.03148 (18)	0.02537 (18)	0.01196 (12)	0.00214 (11)	-0.00380 (10)
O1	0.0505 (12)	0.0469 (12)	0.0215 (10)	0.0198 (9)	-0.0049 (9)	0.0034 (9)
O2	0.0507 (12)	0.0585 (13)	0.0175 (9)	0.0199 (10)	-0.0031 (8)	-0.0034 (9)
O3	0.0535 (13)	0.0409 (11)	0.0290 (11)	-0.0047 (10)	-0.0110 (10)	0.0079 (9)
C1	0.0292 (13)	0.0285 (13)	0.0206 (12)	-0.0021 (10)	-0.0026 (10)	0.0029 (10)
C2	0.0261 (12)	0.0261 (12)	0.0170 (11)	-0.0032 (10)	-0.0007 (9)	0.0037 (9)
C3	0.0299 (13)	0.0239 (12)	0.0189 (11)	0.0015 (10)	0.0031 (10)	-0.0006 (9)
C4	0.0307 (13)	0.0272 (12)	0.0204 (12)	0.0050 (10)	-0.0011 (10)	0.0044 (10)
C5	0.0386 (15)	0.0414 (15)	0.0310 (14)	0.0065 (12)	-0.0030 (12)	0.0062 (12)

Geometric parameters (\AA , $^\circ$)

Br1—C3	1.894 (2)	C2—C3	1.392 (3)
O1—H1	0.825 (10)	C2—C4 ⁱ	1.394 (3)
O1—C1	1.303 (3)	C3—C4	1.377 (3)
O2—C1	1.207 (3)	C4—H4	0.9300
O3—H3	0.817 (10)	C5—C5 ⁱⁱ	1.493 (5)

O3—C5	1.428 (4)	C5—H5A	0.9700
C1—C2	1.504 (3)	C5—H5B	0.9700
C1—O1—H1	112 (3)	C4—C3—C2	120.5 (2)
C5—O3—H3	108 (3)	C2 ⁱ —C4—H4	119.1
O1—C1—C2	112.1 (2)	C3—C4—C2 ⁱ	121.9 (2)
O2—C1—O1	123.7 (2)	C3—C4—H4	119.1
O2—C1—C2	124.1 (2)	O3—C5—C5 ⁱⁱ	110.6 (3)
C3—C2—C1	124.6 (2)	O3—C5—H5A	109.5
C3—C2—C4 ⁱ	117.6 (2)	O3—C5—H5B	109.5
C4 ⁱ —C2—C1	117.8 (2)	C5 ⁱⁱ —C5—H5A	109.5
C2—C3—Br1	124.11 (18)	C5 ⁱⁱ —C5—H5B	109.5
C4—C3—Br1	115.39 (18)	H5A—C5—H5B	108.1
O3—C5—C5 ⁱⁱ —O3 ⁱⁱ	180.000 (1)		

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

Hydrogen-bond geometry (Å, °)

<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>
O1—H1 \cdots O3	0.83 (1)	1.75 (1)	2.559 (3)	165 (4)
O3—H3 \cdots O2 ⁱⁱⁱ	0.82 (1)	1.97 (1)	2.767 (3)	166 (4)

Symmetry code: (iii) $-x+2, -y+1, -z+2$.