

Crystal structure and Hirshfeld surface analysis of a new dithioglycoluril: 1,4-bis(4-methoxyphenyl)-3a-methyltetrahydroimidazo[4,5-d]imidazole-2,5(1*H*,3*H*)-dithione

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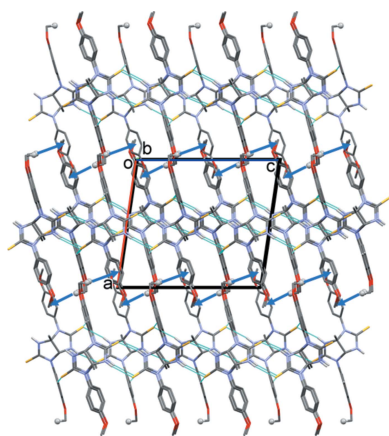
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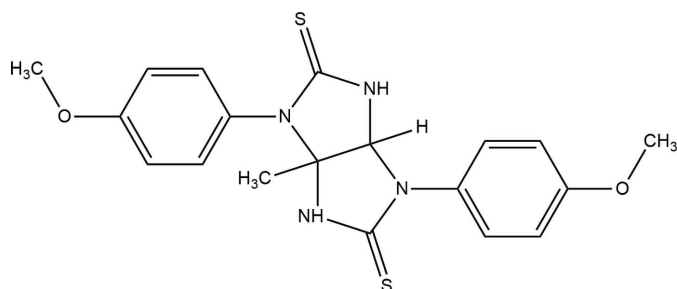
In the title dithioglycoluril derivative, C₁₉H₂₀N₄O₃S₂, there is a difference in the torsion angles between the thioimidazole moiety and the methoxyphenyl groups on either side of the molecule [C—N—C_{ar}—C_{ar} = 116.9 (2) and −86.1 (3)°, respectively]. The N—C—N bond angle on one side of the dithioglycoluril moiety is slightly smaller compared to that on the opposite side, [110.9 (2)° *cf.* 112.0 (2)°], probably as a result of the steric effect of the methyl group. In the crystal, N—H···S hydrogen bonds link adjacent molecules to form chains propagating along the *c*-axis direction. The chains are linked by C—H···S hydrogen bonds, forming layers parallel to the *bc* plane. The layers are then linked by C—H··· π interactions, leading to the formation of a three-dimensional supramolecular network. Hirshfeld surface analysis and two-dimensional fingerprint plots were used to investigate the molecular interactions in the crystal.

1. Chemical context

Heterocycles with five-membered rings containing two nitrogen atoms in the 1,3 positions and three carbon atoms in the ring are known as imidazoles. Most imidazoles, except for the N-substituted derivatives, have a distinct pyrrole type and pyridine-type annular nitrogen atoms. The isolation of imidazole derivatives has been documented (Beyer *et al.*, 2011; Zeng *et al.*, 2003; Dawood *et al.*, 2010). Glycolurils, tetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-diones, are well-known imidazole derivatives of great research interest. As well as serving as building blocks in the preparation of many organic compounds and supramolecular synthons (Burnett *et al.*, 2003; Kravchenko *et al.*, 2018), they have also been reported to behave as nootropic (Ryzhkina *et al.*, 2013), neurotropic (Berlyand *et al.*, 2013) and anxiolytic agents (Kravchenko *et al.*, 2018). Some derivatives are used as flame-resistant materials (Sal'keeva *et al.*, 2016; Zharkov *et al.*, 2015) and gelators (Tiefenbacher *et al.*, 2011). While several glycoluril analogues have been synthesized and characterized, reports on dithioglycolurils are quite rare. In the course of our search for thioureas with bioactivity, we had intended to isolate (2*E*)-*N*-[(4-methoxyphenyl)carbamoithioyl]-3-phenylprop-2-enamide using well-documented methods (Asegbeloyin *et al.*, 2018; Douglass & Dains, 1934; Oyeka *et al.*, 2018); however, we obtained crystals of 1,4-bis(4-methoxyphenyl)-



3*a*-methyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dithione, a new dithioglycoluril. As a result of the importance of glucolurils and their analogues and our current interest in the construction of novel heterocycles with good bioactivity (Asegbeloyin *et al.*, 2019), we decided to investigate the title compound, and we report herein on its synthesis, crystal structure and Hirshfeld surface analysis.



2. Structural commentary

The molecular structure and conformation of the title compound is shown in Fig. 1. The two imidazole rings, N1/N2/C1–C3 and N3/N4/C2/C3/C5, are inclined to each other by 62.16 (12)°, while the 4-methoxyphenyl rings (C6–C11 and C13–C18) are inclined to each other by 29.36 (12)°. The latter rings are inclined to the imidazole ring to which they are attached by 62.51 (11) and 89.16 (12)°, respectively. Hence, the two ends of the molecule are orientated differently, as shown by the difference in the torsion angles between the thioimidazole moiety and the methoxyphenyl groups; C2–N3–C6–C11 and C3–N1–C13–C14 are 116.9 (2) and –86.1 (3)°, respectively.

The thione C=S bond lengths of 1.674 (2) Å are longer than those in previous reports where all N atoms were substituted (Deng *et al.*, 2010; Wang *et al.*, 2011; Wu & Sun, 2009; Zhang *et al.*, 2011). The C–N bonds around the thione moiety [C1–N1, C1–N2, C5–N3 and C5–N4 = 1.350 (3), 1.357 (3), 1.355 (3) and 1.353 (3) Å, respectively] are significantly shorter than the average C–N single bond length of 1.48 Å (Oyeka *et al.*, 2018), as has also been observed in other thioglycoluril systems (Wu & Sun, 2009; Zhang *et al.*, 2011) and acyl thiourea derivatives (Asegbeloyin *et al.*, 2018; Oyeka *et al.*, 2018). This is probably due to the conjugation between the π -electrons on C=S and the lone pairs of electrons on the nitrogen atoms. The C–C bond lengths of the aromatic rings

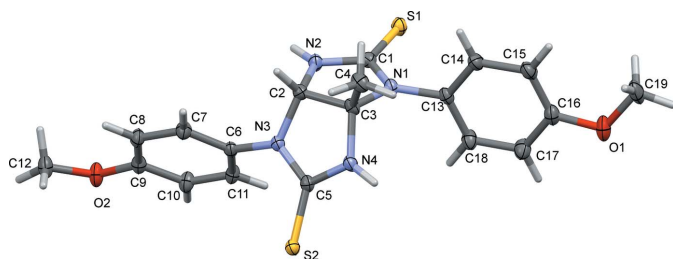


Figure 1

A view of the molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

Table 1

Hydrogen-bond geometry (Å, °).

C_g is the centroid of the C13–C18 ring.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H2...S2 ⁱ	0.86	2.62	3.265 (2)	133
N4–H4...S1 ⁱⁱ	0.86	2.57	3.382 (2)	157
C7–H7...S1 ⁱⁱⁱ	0.93	2.87	3.786 (3)	170
C12–H12 <i>B</i> ...C _g ^{iv}	0.96	2.99	3.893 (3)	157

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

are typical of sp^2 -hybridized carbons while the C2–C3 bond of the thioglycoluril moiety [1.542 (3) Å] shows sp^3 hybridization. These bond lengths are consistent with previous reports for thioglycolurils and acylthioureas (Binzet *et al.*, 2009; Oyeka *et al.*, 2018; Wang & Xi, 2009; Yang, 2010). The imidazole carbon atoms, C2 and C3, each have a distorted tetrahedral geometry with the N1–C3–N4 and N2–C2–N3 bond angles being 112.0 (4) and 112.9 (2)°, respectively. The bond angles between the N-methoxyphenyl nitrogen atom and the aromatic ring, C5–N3–C6 and C1–N1–C13, are 124.8 (2) and 126.1 (2)°, respectively.

3. Supramolecular features

In the crystal, N–H...S hydrogen bonds link neighbouring molecules to form chains propagating along the *c*-axis direction (Table 1 and Fig. 2). The chains are linked by C–H...S hydrogen bonds, forming layers parallel to the *bc* plane (Fig. 3 and Table 1). In turn, the layers are linked by C–H... π interactions involving a methoxy methyl H atom (H12*B*) and a 4-methoxyphenyl ring (C13–C18); see Table 1. These interactions result in the formation of a supramolecular three-dimensional architecture (Fig. 3).

3.1. Hirshfeld Surface Analysis

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed with *Crystal-Explorer17* (Turner *et al.*, 2017). In the Hirshfeld surface

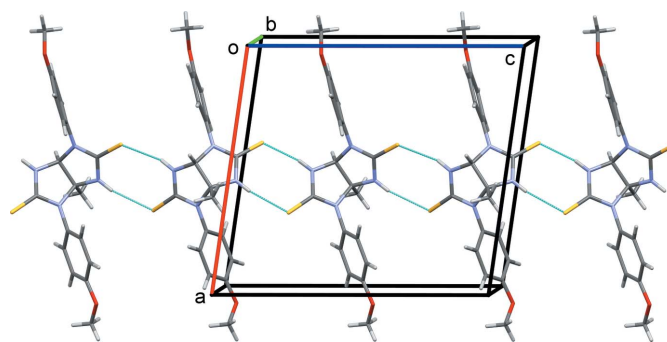
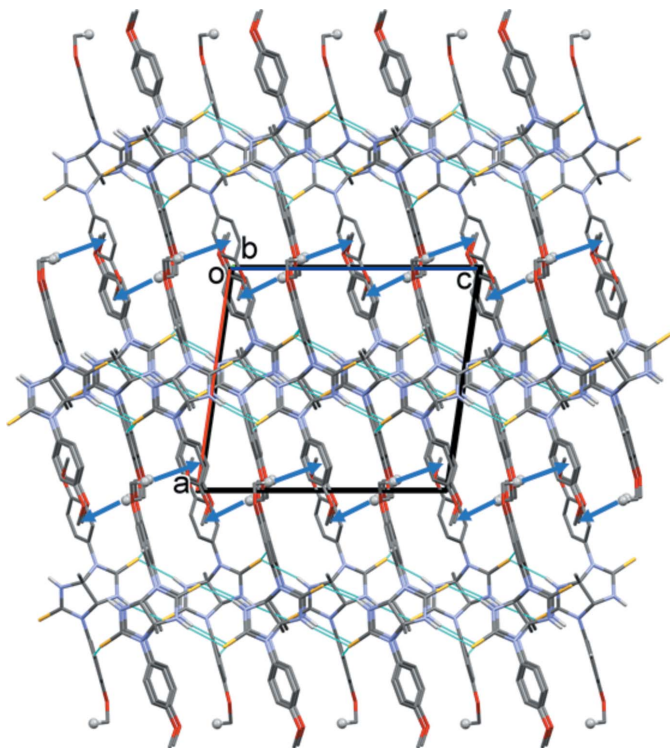


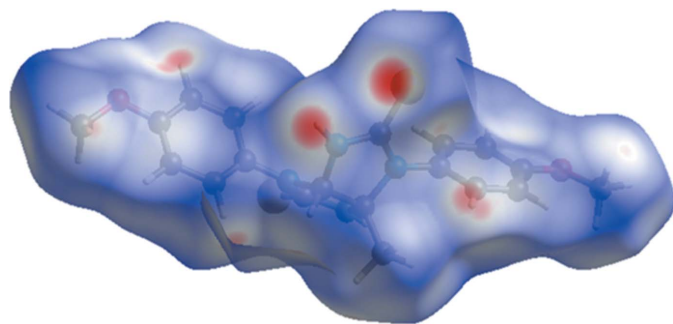
Figure 2

A view along the *b* axis of the N–H...S hydrogen-bonded chain in the crystal of the title compound.


Figure 3

A view along the b axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines and the $C-H \cdots \pi$ interactions are represented by blue arrows (see Table 1 for details). For clarity, H atoms not involved in these interactions have been omitted.

mapped over d_{norm} (Fig. 4), the red spots indicate contacts shorter than the sum of the van der Waals radii with negative d_{norm} , blue regions represent contacts longer than the sum of van der Waals radii with negative d_{norm} , while white regions correspond to intermolecular distances close to the sum of the van der Waals radii with d_{norm} equal to zero. The most intense red spots on the surface of the title compound are found around the thione S and N–H groups of the compound, which play a role in the hydrogen bonding interactions in the crystal (Table 1 and Fig. 2). The less intense red spots (Fig. 4), are observed around the ring carbon atoms resulting from $C-H \cdots S$ and $C-H \cdots \pi$ short contacts. The two-dimensional

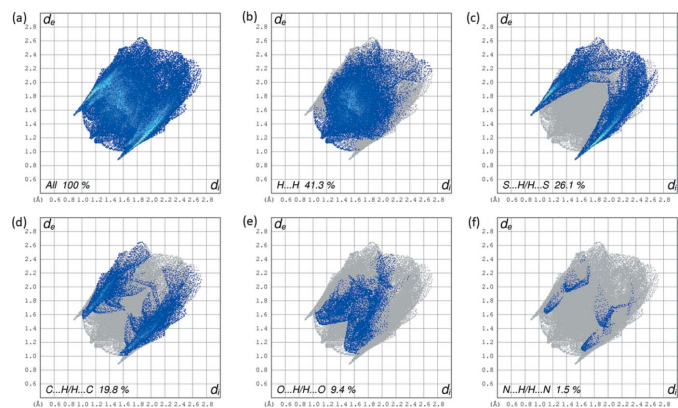

Figure 4

The Hirshfeld surface of the title compound mapped over d_{norm} , with an arbitrary colour scale of -0.3207 to 1.4281 .

fingerprint plots (Fig. 5) show the overall contribution of the various interactions and those delineated into $H \cdots H$, $S \cdots H/H \cdots S$, $C \cdots H/H \cdots C$, $O \cdots H/H \cdots O$ and $N \cdots H/H \cdots N$ contacts. Apart from the non-directional $H \cdots H$ contacts (41.3%), the highest contribution to the Hirshfeld surface is from $S \cdots H/H \cdots S$ contacts (26.1%).

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.39, February 2019) for thioglycoluril found two molecules similar to the title compound: 1,6-divaloyl-3,3a,4,6a-tetramethyltetrahydroimidazo[4,5- d]imidazole-2,5-(1*H*,3*H*)-dithione (refcode ADEMOL; Duspara *et al.*, 2001) and 1,6-diacetyl-3,4,7,8-tetramethyl-2,5-dithioglycoluril (SOLQIT; Cow, 1998). In both compounds, large polar groups are substituted on adjacent sides of the imidazole ring, resulting in steric hindrance and distortion of the $C-N-C$ angles. The $C-N-C$ bond angles between the thione carbon and the N-substituted groups are *ca* 119.8 and 125.4° in ADEMOL and 122.6 and 125.4° in SOLQIT. In the title compound, the $C5-N3-C6$ and $C1-N1-C13$ bond angles are 124.8 (2) and 126.1 (2) $^\circ$, respectively, showing only little distortion. The thione bond lengths [$C5=S2$ and $C1=S1$ are both 1.674 (2) Å] in the title compound are longer than in the reference compounds (1.650 – 1.664 Å). This is probably due to the fact that all of the imidazole nitrogen atoms in the reference compounds are substituted. The presence of unsubstituted imidazole nitrogens in the title compound promotes conjugation between the lone pairs of electrons on the nitrogen atom and the $C=S$ π -electrons and hence stretches the $C=S$ bond. The $C-N$ bond lengths around the thione group of the title compound [1.350 (3)– 1.357 (3) Å] are shorter than the corresponding bonds in the reference compounds (*ca* 1.367 – 1.397 Å). The other $C-N$ bonds and the $C-C$ bonds in the thioglycoluril moiety are similar to those of the title compound.


Figure 5

(a) The full two-dimensional fingerprint plot of the title compound, and fingerprint plots delineated into (b) $H \cdots H$, (c) $S \cdots H/H \cdots S$, (d) $C \cdots H/H \cdots C$, (e) $O \cdots H/H \cdots O$ and (f) $N \cdots H/H \cdots N$ contacts.

5. Synthesis and crystallization

The title compound was synthesized according to the reported method (Asegbeloyin *et al.*, 2018; Douglass & Dains, 1934; Oyeka *et al.*, 2018). A solution of cinnamoyl chloride (0.02 mol) dissolved in 40 ml acetone was mixed with a 30 ml acetone solution of potassium thiocyanate (0.02 mol). The reaction mixture was refluxed for 30 min to give a suspension of cinnamoyl isothiocyanate, which was then left to cool to room temperature. 4-Methoxyaniline (0.02 mol) was dissolved in 40 ml of acetone and the resulting solution was mixed with the suspension of cinnamoyl isothiocyanate, and the mixture was stirred for 2 h. The resultant lemon-green solution was filtered and left at room temperature for 96 h to obtain colourless plate-like crystals of the title compound.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were placed at idealized positions (N–H = 0.86 Å, C–H = 0.93–0.98 Å) and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C-methyl})$ and $1.2U_{\text{eq}}(\text{C,N})$ for other H atoms.

Acknowledgements

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References

Asegbeloyin, J. N., Izuoguo, D. C., Oyeka, E. E., Okpareke, O. C. & Ibezim, A. (2019). *J. Mol. Struct.* **1175**, 219–229.
 Asegbeloyin, J. N., Oyeka, E. E., Okpareke, O. & Ibezim, A. (2018). *J. Mol. Struct.* **1153**, 69–77.
 Berlyand, A. S., Lebedev, O. V. & Prokopov, A. A. (2013). *Pharm. Chem. J.* **47**, 176–178.
 Beyer, A., Reucher, C. M. M. & Bolm, C. (2011). *Org. Lett.* **13**, 2876–2879.
 Binzet, G., Külcü, N., Flörke, U. & Arslan, H. (2009). *J. Coord. Chem.* **62**, 3454–3462.
 Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst.* **A71**, 59–75.
 Burnett, C. A., Lagona, J., Wu, A., Shaw, J. A., Coody, D., Fettinger, J. C., Day, A. I. & Isaacs, L. (2003). *Tetrahedron*, **59**, 1961–1970.
 Cow, C. N. (1998). *Chem. Commun.* pp. 1147–1148.
 Dawood, K. M., Elwan, N. M., Farahat, A. A. & Abdel-Wahab, B. F. (2010). *J. Heterocycl. Chem.* **47**, 243–267.
 Deng, C., Shu, W. & Zhang, D. (2010). *Acta Cryst.* **E66**, o1524.
 Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
 Douglass, I. B. & Dains, F. (1934). *J. Am. Chem. Soc.* **56**, 719–721.
 Duspara, P. A., Matta, C. F., Jenkins, S. I. & Harrison, P. H. (2001). *Org. Lett.* **3**, 495–498.
 Kravchenko, A. N., Baranov, V. V. & Gazieva, G. A. (2018). *Russ. Chem. Rev.* **87**, 89–108.
 Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
 McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₉ H ₂₀ N ₄ O ₂ S ₂
M_r	400.51
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	13.1955 (3), 10.0157 (2), 14.5476 (3)
β (°)	98.329 (2)
V (Å ³)	1902.36 (7)
Z	4
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	2.73
Crystal size (mm)	0.12 × 0.05 × 0.01
Data collection	
Diffractometer	Rigaku Oxford Diffraction XtaLAB Synergy, Dualflex, Pilatus 200K
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)
$T_{\text{min}}, T_{\text{max}}$	0.735, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25390, 3824, 3267
R_{int}	0.053
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.624
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.047, 0.156, 1.22
No. of reflections	3824
No. of parameters	247
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.63, -0.53

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *olex2.solve* (Bourhis *et al.*, 2015), *SHELXL2016/6* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

Oyeka, E. E., Asegbeloyin, J. N., Babahan, I., Eboma, B., Okpareke, O., Lane, J., Ibezim, A., Bıyık, H. H., Törün, B. & Izuoguo, D. C. (2018). *J. Mol. Struct.* **1168**, 153–164.
 Rigaku OD (2018). Rigaku Oxford Diffraction, Yarnton, England.
 Ryzhkina, I. S., Kiseleva, Y. V., Mishina, O. A., Timosheva, A. P., Sergeeva, S. Y., Kravchenko, A. N. & Kononov, A. I. (2013). *Mendeleev Commun.* **23**, 262–264.
 Sal'keeva, L., Bakibaev, A. A., Khasenova, G., Taishibekova, Y. K., Sugralina, L., Minaeva, Y. V. & Sal'keeva, A. (2016). *Russ. J. Appl. Chem.* **89**, 132–139.
 Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
 Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
 Tiefenbacher, K., Dube, H., Ajami, D. & Rebek, J. (2011). *Chem. Commun.* **47**, 7341–7343.
 Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia. <http://hirshfeldsurface.net>
 Wang, M., Wang, J. & Xiang, J. (2011). *Acta Cryst.* **E67**, o2060.
 Wang, Z. & Xi, H. (2009). *Acta Cryst.* **E65**, o1426.
 Wu, Y. & Sun, Y. (2009). *Acta Cryst.* **E65**, o1715.
 Yang, Y. (2010). *Acta Cryst.* **E66**, o1673.
 Zeng, R.-S., Zou, J.-P., Zhi, S.-J., Chen, J. & Shen, Q. (2003). *Org. Lett.* **5**, 1657–1659.
 Zhang, Q., Li, P., Chen, X., Wang, X. & Liu, H. (2011). *Acta Cryst.* **E67**, o1673.
 Zharkov, M. N., Kuchurov, I. V., Fomenkov, I. V., Zlotin, S. G. & Tartakovsky, V. A. (2015). *Mendeleev Commun.* **25**, 15–16.

supporting information

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Crystal structure and Hirshfeld surface analysis of a new dithioglycoluril: 1,4-bis(4-methoxyphenyl)-3a-methyltetrahydroimidazo[4,5-d]imidazole-2,5(1*H*,3*H*)-dithione

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: *olex2.solve* (Bourhis *et al.*, 2015); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

1,4-Bis(4-methoxyphenyl)-3a-methyltetrahydroimidazo[4,5-d]imidazole-2,5(1*H*,3*H*)-dithione

Crystal data

C₁₉H₂₀N₄O₂S₂

M_r = 400.51

Monoclinic, *P*2₁/*c*

a = 13.1955 (3) Å

b = 10.0157 (2) Å

c = 14.5476 (3) Å

β = 98.329 (2)°

V = 1902.36 (7) Å³

Z = 4

F(000) = 840

D_x = 1.398 Mg m⁻³

Cu *Kα* radiation, λ = 1.54184 Å

Cell parameters from 11825 reflections

θ = 3.4–73.8°

μ = 2.73 mm⁻¹

T = 100 K

Plate, clear colourless

0.12 × 0.05 × 0.01 mm

Data collection

Rigaku Oxford Diffraction XtaLAB Synergy,
Dualflex, Pilatus 200K
diffractometer

Radiation source: micro-focus sealed X-ray
tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

ω scans

Absorption correction: multi-scan
(*CrysAlisPro*; Rigaku OD, 2018)

T_{min} = 0.735, *T_{max}* = 1.000

25390 measured reflections

3824 independent reflections

3267 reflections with *I* > 2σ(*I*)

R_{int} = 0.053

θ_{max} = 74.2°, θ_{min} = 3.4°

h = -16→15

k = -12→12

l = -18→15

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.047

wR(*F*²) = 0.156

S = 1.22

3824 reflections

247 parameters

0 restraints

Primary atom site location: iterative

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$$

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

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

$$\Delta\rho_{\max} = 0.63 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.53 \text{ e } \text{\AA}^{-3}$$

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
S2	0.42015 (4)	0.63758 (5)	0.56357 (4)	0.02883 (19)
S1	0.69303 (4)	0.64039 (6)	0.20550 (4)	0.03272 (19)
O2	0.05235 (12)	0.52239 (19)	0.24656 (13)	0.0411 (4)
O1	1.06251 (13)	0.6869 (2)	0.55605 (14)	0.0501 (5)
N3	0.42969 (13)	0.73812 (19)	0.39262 (13)	0.0282 (4)
N1	0.66847 (13)	0.76111 (19)	0.36715 (13)	0.0282 (4)
N4	0.56744 (13)	0.7746 (2)	0.49428 (13)	0.0302 (4)
H4	0.607926	0.773181	0.546222	0.036*
N2	0.52813 (13)	0.7489 (2)	0.26451 (13)	0.0321 (4)
H2	0.488712	0.728354	0.214118	0.039*
C6	0.33311 (15)	0.6860 (2)	0.35217 (14)	0.0278 (4)
C5	0.47370 (15)	0.7169 (2)	0.48150 (15)	0.0269 (4)
C13	0.77144 (15)	0.7412 (2)	0.41232 (15)	0.0285 (5)
C2	0.49454 (16)	0.8198 (2)	0.34048 (15)	0.0288 (5)
H2A	0.462130	0.905134	0.320659	0.035*
C9	0.14274 (16)	0.5846 (2)	0.27955 (16)	0.0326 (5)
C1	0.62924 (16)	0.7179 (2)	0.28148 (15)	0.0290 (4)
C3	0.59244 (16)	0.8391 (2)	0.41109 (16)	0.0294 (5)
C11	0.31898 (16)	0.5490 (2)	0.34585 (16)	0.0326 (5)
H11	0.373181	0.491552	0.365398	0.039*
C10	0.22374 (17)	0.4982 (2)	0.31029 (17)	0.0355 (5)
H10	0.213660	0.406289	0.306848	0.043*
C8	0.15769 (17)	0.7205 (3)	0.28276 (17)	0.0346 (5)
H8	0.104211	0.778010	0.261024	0.041*
C7	0.25360 (17)	0.7716 (3)	0.31882 (17)	0.0345 (5)
H7	0.264271	0.863400	0.320503	0.041*
C14	0.84562 (18)	0.8354 (3)	0.40334 (17)	0.0370 (5)
H14	0.829035	0.910173	0.366309	0.044*
C16	0.96858 (17)	0.7111 (3)	0.50581 (18)	0.0383 (6)
C15	0.94482 (18)	0.8197 (3)	0.44908 (17)	0.0393 (6)
H15	0.994904	0.882321	0.441325	0.047*
C18	0.79544 (19)	0.6308 (2)	0.4673 (2)	0.0383 (6)
H18	0.745801	0.566657	0.473044	0.046*
C4	0.62578 (19)	0.9834 (3)	0.42760 (19)	0.0391 (6)

H4A	0.685302	0.986734	0.474091	0.059*
H4B	0.571319	1.033392	0.448355	0.059*
H4C	0.641782	1.021121	0.370769	0.059*
C12	-0.03793 (18)	0.6032 (3)	0.2306 (2)	0.0427 (6)
H12A	-0.033051	0.663519	0.180189	0.064*
H12B	-0.044452	0.653243	0.285733	0.064*
H12C	-0.096868	0.546930	0.215268	0.064*
C17	0.8940 (2)	0.6156 (3)	0.5143 (2)	0.0432 (6)
H17	0.910343	0.541071	0.551726	0.052*
C19	1.14391 (19)	0.7756 (4)	0.5431 (2)	0.0588 (9)
H19A	1.151078	0.778830	0.478399	0.088*
H19B	1.206604	0.744313	0.578239	0.088*
H19C	1.128777	0.863354	0.563931	0.088*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0231 (3)	0.0352 (3)	0.0281 (3)	-0.00311 (18)	0.0035 (2)	0.00066 (19)
S1	0.0274 (3)	0.0385 (3)	0.0323 (3)	0.0050 (2)	0.0046 (2)	-0.0049 (2)
O2	0.0238 (8)	0.0425 (10)	0.0540 (11)	0.0022 (7)	-0.0052 (7)	-0.0128 (8)
O1	0.0242 (8)	0.0612 (13)	0.0617 (12)	0.0036 (8)	-0.0043 (8)	-0.0093 (10)
N3	0.0207 (8)	0.0359 (10)	0.0283 (9)	-0.0014 (7)	0.0043 (7)	0.0021 (7)
N1	0.0203 (8)	0.0334 (10)	0.0313 (9)	0.0005 (7)	0.0049 (7)	-0.0038 (7)
N4	0.0218 (8)	0.0410 (11)	0.0281 (9)	-0.0041 (7)	0.0050 (7)	-0.0020 (8)
N2	0.0223 (8)	0.0439 (11)	0.0298 (10)	0.0034 (8)	0.0028 (7)	-0.0014 (8)
C6	0.0218 (10)	0.0368 (12)	0.0245 (10)	0.0012 (8)	0.0031 (8)	-0.0011 (9)
C5	0.0219 (9)	0.0290 (10)	0.0299 (10)	0.0014 (8)	0.0037 (8)	-0.0034 (8)
C13	0.0230 (10)	0.0336 (11)	0.0294 (11)	-0.0037 (8)	0.0055 (8)	-0.0073 (9)
C2	0.0253 (10)	0.0321 (11)	0.0298 (11)	0.0019 (8)	0.0069 (8)	0.0021 (9)
C9	0.0251 (11)	0.0397 (12)	0.0319 (11)	0.0037 (9)	0.0006 (8)	-0.0074 (9)
C1	0.0279 (10)	0.0298 (10)	0.0295 (11)	-0.0001 (8)	0.0055 (8)	0.0012 (8)
C3	0.0261 (10)	0.0322 (11)	0.0318 (11)	-0.0005 (8)	0.0101 (8)	-0.0035 (9)
C11	0.0248 (10)	0.0362 (12)	0.0349 (12)	0.0074 (9)	-0.0020 (8)	-0.0034 (9)
C10	0.0291 (11)	0.0322 (12)	0.0430 (13)	0.0016 (9)	-0.0027 (9)	-0.0046 (10)
C8	0.0251 (10)	0.0397 (13)	0.0378 (12)	0.0081 (9)	0.0012 (9)	0.0006 (10)
C7	0.0286 (11)	0.0341 (12)	0.0397 (12)	0.0022 (9)	0.0010 (9)	0.0007 (10)
C14	0.0289 (11)	0.0451 (13)	0.0368 (12)	-0.0083 (10)	0.0041 (9)	0.0045 (10)
C16	0.0259 (11)	0.0487 (14)	0.0395 (13)	0.0019 (10)	0.0018 (9)	-0.0091 (11)
C15	0.0282 (11)	0.0519 (15)	0.0387 (13)	-0.0098 (10)	0.0074 (9)	-0.0026 (11)
C18	0.0281 (11)	0.0340 (12)	0.0517 (15)	-0.0039 (9)	0.0020 (10)	-0.0011 (10)
C4	0.0382 (12)	0.0334 (12)	0.0478 (14)	-0.0015 (10)	0.0128 (10)	-0.0048 (10)
C12	0.0240 (11)	0.0507 (15)	0.0518 (15)	0.0035 (10)	0.0002 (10)	-0.0070 (12)
C17	0.0343 (13)	0.0375 (13)	0.0557 (16)	0.0026 (10)	-0.0005 (11)	0.0040 (11)
C19	0.0237 (12)	0.103 (3)	0.0501 (16)	-0.0083 (14)	0.0054 (11)	-0.0106 (16)

Geometric parameters (Å, °)

S2—C5	1.674 (2)	C9—C8	1.375 (4)
S1—C1	1.674 (2)	C3—C4	1.520 (3)
O2—C9	1.370 (3)	C11—H11	0.9300
O2—C12	1.431 (3)	C11—C10	1.385 (3)
O1—C16	1.366 (3)	C10—H10	0.9300
O1—C19	1.427 (4)	C8—H8	0.9300
N3—C6	1.423 (3)	C8—C7	1.395 (3)
N3—C5	1.355 (3)	C7—H7	0.9300
N3—C2	1.472 (3)	C14—H14	0.9300
N1—C13	1.435 (3)	C14—C15	1.389 (3)
N1—C1	1.350 (3)	C16—C15	1.374 (4)
N1—C3	1.487 (3)	C16—C17	1.391 (4)
N4—H4	0.8600	C15—H15	0.9300
N4—C5	1.353 (3)	C18—H18	0.9300
N4—C3	1.451 (3)	C18—C17	1.388 (4)
N2—H2	0.8600	C4—H4A	0.9600
N2—C2	1.437 (3)	C4—H4B	0.9600
N2—C1	1.357 (3)	C4—H4C	0.9600
C6—C11	1.386 (3)	C12—H12A	0.9600
C6—C7	1.387 (3)	C12—H12B	0.9600
C13—C14	1.379 (3)	C12—H12C	0.9600
C13—C18	1.374 (3)	C17—H17	0.9300
C2—H2A	0.9800	C19—H19A	0.9600
C2—C3	1.542 (3)	C19—H19B	0.9600
C9—C10	1.398 (3)	C19—H19C	0.9600
C9—O2—C12	117.5 (2)	C10—C11—H11	120.2
C16—O1—C19	117.4 (2)	C9—C10—H10	119.9
C6—N3—C2	122.93 (17)	C11—C10—C9	120.1 (2)
C5—N3—C6	124.84 (18)	C11—C10—H10	119.9
C5—N3—C2	112.21 (17)	C9—C8—H8	120.2
C13—N1—C3	121.96 (18)	C9—C8—C7	119.6 (2)
C1—N1—C13	126.11 (18)	C7—C8—H8	120.2
C1—N1—C3	111.89 (17)	C6—C7—C8	120.3 (2)
C5—N4—H4	123.6	C6—C7—H7	119.9
C5—N4—C3	112.89 (18)	C8—C7—H7	119.9
C3—N4—H4	123.6	C13—C14—H14	119.7
C2—N2—H2	123.9	C13—C14—C15	120.6 (2)
C1—N2—H2	123.9	C15—C14—H14	119.7
C1—N2—C2	112.18 (18)	O1—C16—C15	124.9 (2)
C11—C6—N3	119.63 (19)	O1—C16—C17	115.4 (2)
C11—C6—C7	120.1 (2)	C15—C16—C17	119.7 (2)
C7—C6—N3	120.3 (2)	C14—C15—H15	120.2
N3—C5—S2	126.03 (16)	C16—C15—C14	119.7 (2)
N4—C5—S2	125.21 (16)	C16—C15—H15	120.2
N4—C5—N3	108.73 (19)	C13—C18—H18	120.1

C14—C13—N1	119.9 (2)	C13—C18—C17	119.7 (2)
C18—C13—N1	120.11 (19)	C17—C18—H18	120.1
C18—C13—C14	119.9 (2)	C3—C4—H4A	109.5
N3—C2—H2A	112.0	C3—C4—H4B	109.5
N3—C2—C3	102.70 (17)	C3—C4—H4C	109.5
N2—C2—N3	112.86 (19)	H4A—C4—H4B	109.5
N2—C2—H2A	112.0	H4A—C4—H4C	109.5
N2—C2—C3	104.61 (17)	H4B—C4—H4C	109.5
C3—C2—H2A	112.0	O2—C12—H12A	109.5
O2—C9—C10	114.6 (2)	O2—C12—H12B	109.5
O2—C9—C8	125.1 (2)	O2—C12—H12C	109.5
C8—C9—C10	120.2 (2)	H12A—C12—H12B	109.5
N1—C1—S1	126.59 (16)	H12A—C12—H12C	109.5
N1—C1—N2	109.29 (19)	H12B—C12—H12C	109.5
N2—C1—S1	124.11 (17)	C16—C17—H17	119.8
N1—C3—C2	101.56 (17)	C18—C17—C16	120.3 (2)
N1—C3—C4	111.68 (18)	C18—C17—H17	119.8
N4—C3—N1	111.96 (19)	O1—C19—H19A	109.5
N4—C3—C2	103.31 (17)	O1—C19—H19B	109.5
N4—C3—C4	112.76 (19)	O1—C19—H19C	109.5
C4—C3—C2	114.8 (2)	H19A—C19—H19B	109.5
C6—C11—H11	120.2	H19A—C19—H19C	109.5
C10—C11—C6	119.7 (2)	H19B—C19—H19C	109.5

Hydrogen-bond geometry (Å, °)C_g is the centroid of the C13–C18 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...S2 ⁱ	0.86	2.62	3.265 (2)	133
N4—H4...S1 ⁱⁱ	0.86	2.57	3.382 (2)	157
C7—H7...S1 ⁱⁱⁱ	0.93	2.87	3.786 (3)	170
C12—H12B...C _g ^{iv}	0.96	2.99	3.893 (3)	157

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