# Crystal structure of 2,6-dibenzylpyrrolo[3,4-f]-isoindole-1,3,5,7(2H,6H)-tetrathione

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The title compound, $C_{24}H_{16}N_2S_4$, consists of a central pyromellitic diimide substituted with an S atom and terminal benzyl groups. The molecule lies on a crystallographic inversion centre so that the asymmetric unit contains half of the molecule. The molecule was prepared by thionation of N,N'-dibenzyl-pyromellitic diimide with Lawesson's reagent and has an S-shaped conformation similar to other compounds of this type. The phenyl groups are tilted by 72.69 (8)° with respect to the plane of the central arene ring. In the crystal, molecules are connected by C—H···π interactions and weak short S···S contacts, forming supramolecular layers extending paralled to the ab plane. The crystal studied was found to be non-merohedrally twinned, with the minor component being 0.113 (3).

1. Chemical context

Recently, pyromellitic diimide derivatives have been spotlighted due to their use in energy-storage materials (Nalluri et al. 2016). They also show potential applications in photovoltaic devices (Kanosue et al., 2016) and organic semiconductors (Zheng et al., 2008). Not only pyromellitic diimide derivatives, but also pyromellitic diimides substituted with sulfur have potential applications in organic semiconductors (Yang et al., 2015). We have reported copper(I) coordination polymers based on pyromellitic diimide derivatives (Park et al., 2011), which showed colour change owing to intermolecular halogen–π interactions. In addition, we have found that reversible solvent exchange and crystal transformations were possible in the crystals (Kang et al., 2015). In an extension of previous research, we have synthesized the pyromellitic diimide in which the O atoms are replaced with S atoms, by the reaction of N,N'-dibenzylpyromellitic diimide with Lawesson's reagent, and report its crystal structure here.
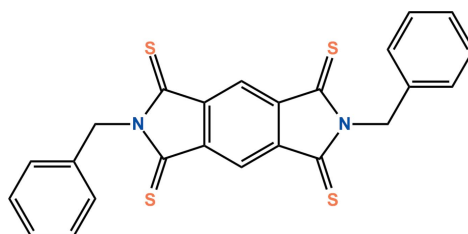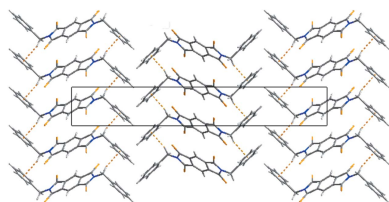
2. Structural commentary

The molecular structure of the title compound consists of a central pyromellitic diimide substituted with S atoms and two terminal benzyl groups (Fig. 1). The molecule possesses a crystallographic inversion centre and thus the asymmetric unit

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

$Cg1$ is the centroid of the C7–C12 ring.

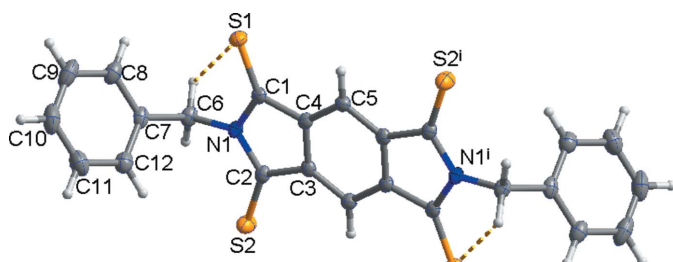| D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6$B$$\cdots$S2	0.99	2.75	3.208 (3)	109
C6—H6$B$$\cdots$$Cg1^i$	0.99	2.66	3.498 (3)	142

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

Figure 1
The asymmetric unit of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius and yellow dashed lines represent intramolecular C—H$\cdots$S short contacts. Unlabelled atoms are generated by the symmetry operation ($-x + 2, -y + 1, -z$).

of the title compound is composed of half a molecule. The molecule exhibits an intramolecular C6—H6$B$$\cdots$S2 short contact (Table 1). In the molecule, the terminal phenyl groups point in opposite directions and their planes are tilted by 72.69 (8)° with respect to the plane of the central arene ring, forming an elongated S-shaped molecule.

3. Supramolecular features

In the crystal, C6—H6$B$$\cdots$$Cg1^i$ ($Cg1$ is the centroid of the C7–C12 ring) interactions between neighbouring molecules generate a one-dimensional loop chain (yellow dashed lines in Fig. 2, and Table 1). Moreover, adjacent molecules are connected by a weak short S1$\cdots$ S2 contact [3.5921 (10) Å], resulting in the formation of a two-dimensional network (yellow and black dashed lines in Fig. 3).
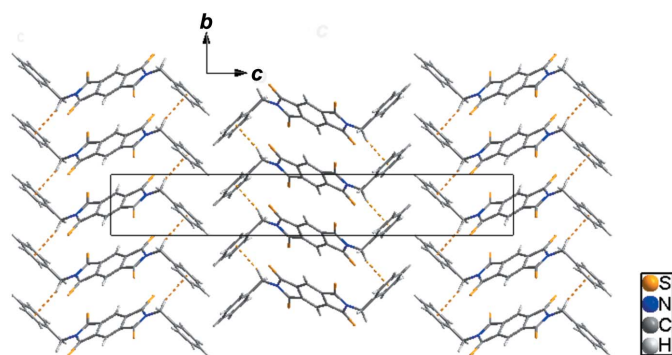

Figure 2
Intermolecular C—H$\cdots$$\pi$ interactions (yellow dashed lines) forming one-dimensional loop chains.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{24}H_{16}N_2S_4$
M_r	460.63
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	6.8571 (4), 4.7724 (3), 32.0010 (17)
β (°)	95.916 (4)
V (Å^3)	1041.65 (11)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.47
Crystal size (mm)	0.43 × 0.34 × 0.01
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.646, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1829, 1829, 1640
R_{int}	0.059
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.089, 1.05
No. of reflections	1829
No. of parameters	137
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.23

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2010), *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

4. Synthesis and crystallization

N,*N*′-Dibenzylpyromellitic diimide was synthesized by the reaction of pyromellitic dianhydride with 2-phenylethylamine according to the literature procedure of Im *et al.* (2017). To a stirred solution of *N*,*N*′-dibenzylpyromellitic diimide (0.25 g, 0.63 mmol) in anhydrous toluene (100 ml) was added Lawesson's reagent (2.00 g, 4.90 mmol), and the resulting mixture was stirred under reflux for 36 h. It was then cooled to room temperature and concentrated *in vacuo*, followed by purification by silica-gel flash column chromatography (CH$_2$Cl$_2$–*n*-hexane, 1:3 *v/v*). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane solution of the title compound.
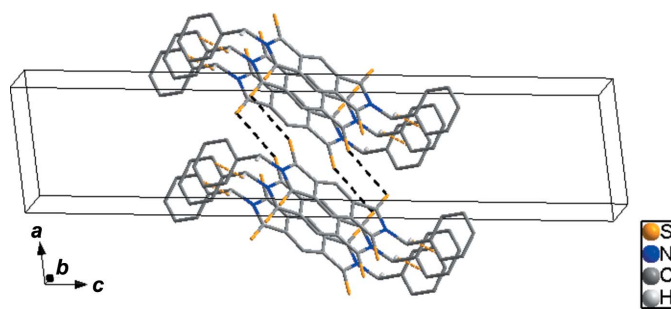

Figure 3
The packing diagram for the title compound, showing the two-dimensional network formed by C—H$\cdots$$\pi$ interactions (yellow dashed lines) and weak short S$\cdots$S contacts (black dashed lines). H atoms not involved in intermolecular interactions have been omitted for clarity.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic C—H groups, and C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for Csp^3—H groups. Non-merohedral twinning was identified in the crystal (TwinRotMat within *PLATON*; Spek, 2009); the twin law is −0.999 0 0.002, 0 −1 0, 1 0 0.999 and the final refined BASF parameter was determined to be 0.113 (3).

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Crystal structure of 2,6-dibenzylpyrrolo[3,4-*f*]isoindole-1,3,5,7(2*H*,6*H*)-tetrathione

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

2,6-Dibenzylpyrrolo[3,4-*f*]isoindole-1,3,5,7(2*H*,6*H*)-tetrathione

Crystal data

$C_{24}H_{16}N_2S_4$	$F(000) = 476$
$M_r = 460.63$	$D_x = 1.469$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.8571$ (4) Å	Cell parameters from 3915 reflections
$b = 4.7724$ (3) Å	$\theta = 2.6–25.5°$
$c = 32.0010$ (17) Å	$\mu = 0.47$ mm^{-1}
$\beta = 95.916$ (4)°	$T = 173$ K
$V = 1041.65$ (11) Å^3	Plate, brown
$Z = 2$	$0.43 \times 0.34 \times 0.01$ mm

Data collection

Bruker APEXII CCD diffractometer	1829 independent reflections
	1640 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.059$
Absorption correction: multi-scan (SADABS; Bruker, 2014)	$\theta_{max} = 25.0°$, $\theta_{min} = 1.3°$
	$h = -8 \rightarrow 8$
$T_{min} = 0.646$, $T_{max} = 0.746$	$k = -5 \rightarrow 5$
1829 measured reflections	$l = -6 \rightarrow 38$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	
$wR(F^2) = 0.089$	$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.6197P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
1829 reflections	$(\Delta/\sigma)_{max} < 0.001$
137 parameters	$\Delta\rho_{max} = 0.26$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.23$ 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.

Refinement. Refined as a 2-component twin

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

	x	y	z	$U_{iso}*/U_{eq}$
S1	0.50612 (10)	0.30438 (16)	0.05735 (2)	0.0259 (2)
S2	1.10897 (11)	0.99091 (17)	0.10558 (2)	0.0299 (2)
N1	0.7913 (3)	0.6607 (5)	0.08677 (6)	0.0192 (5)
C1	0.7132 (4)	0.4707 (6)	0.05665 (7)	0.0189 (6)
C2	0.9678 (4)	0.7718 (6)	0.07722 (7)	0.0199 (6)
C3	1.0046 (4)	0.6467 (6)	0.03656 (7)	0.0182 (6)
C4	0.8521 (4)	0.4592 (6)	0.02468 (7)	0.0184 (6)
C5	1.1572 (4)	0.6945 (6)	0.01231 (7)	0.0199 (6)
H5	1.2604	0.8225	0.0204	0.024*
C6	0.6888 (4)	0.7471 (6)	0.12291 (8)	0.0232 (6)
H6A	0.5503	0.7888	0.1130	0.028*
H6B	0.7493	0.9218	0.1348	0.028*
C7	0.6944 (4)	0.5277 (6)	0.15724 (8)	0.0235 (6)
C8	0.5208 (5)	0.4058 (6)	0.16745 (9)	0.0300 (7)
H8	0.3993	0.4576	0.1525	0.036*
C9	0.5252 (5)	0.2086 (7)	0.19950 (10)	0.0411 (9)
H9	0.4069	0.1252	0.2064	0.049*
C10	0.7023 (5)	0.1345 (7)	0.22125 (9)	0.0423 (9)
H10	0.7052	0.0004	0.2433	0.051*
C11	0.8741 (5)	0.2531 (7)	0.21127 (9)	0.0383 (8)
H11	0.9952	0.2000	0.2263	0.046*
C12	0.8711 (4)	0.4503 (6)	0.17935 (8)	0.0289 (7)
H12	0.9901	0.5326	0.1726	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0227 (3)	0.0291 (4)	0.0261 (3)	−0.0078 (3)	0.0038 (3)	0.0008 (3)
S2	0.0311 (4)	0.0301 (5)	0.0291 (4)	−0.0100 (3)	0.0063 (3)	−0.0092 (3)
N1	0.0213 (11)	0.0168 (13)	0.0198 (10)	−0.0010 (10)	0.0041 (9)	0.0010 (9)
C1	0.0212 (13)	0.0160 (15)	0.0193 (12)	0.0008 (11)	0.0013 (10)	0.0051 (11)
C2	0.0235 (14)	0.0158 (16)	0.0210 (12)	0.0014 (12)	0.0046 (10)	0.0024 (11)
C3	0.0208 (13)	0.0153 (15)	0.0184 (12)	0.0035 (12)	0.0022 (10)	0.0026 (11)
C4	0.0196 (13)	0.0156 (16)	0.0202 (12)	−0.0001 (11)	0.0024 (10)	0.0046 (11)
C5	0.0208 (13)	0.0177 (16)	0.0209 (13)	−0.0005 (12)	0.0012 (10)	0.0021 (11)
C6	0.0279 (14)	0.0180 (17)	0.0249 (13)	0.0020 (12)	0.0089 (11)	−0.0020 (12)
C7	0.0359 (16)	0.0163 (16)	0.0197 (12)	−0.0004 (13)	0.0094 (11)	−0.0036 (11)
C8	0.0359 (16)	0.0259 (19)	0.0304 (15)	−0.0014 (14)	0.0145 (13)	−0.0022 (13)

C9	0.057 (2)	0.029 (2)	0.0427 (17)	−0.0066 (17)	0.0301 (16)	−0.0013 (15)
C10	0.070 (2)	0.032 (2)	0.0276 (16)	−0.0005 (18)	0.0169 (16)	0.0040 (14)
C11	0.053 (2)	0.033 (2)	0.0273 (15)	0.0034 (17)	0.0005 (14)	0.0030 (14)
C12	0.0365 (16)	0.0238 (18)	0.0272 (14)	−0.0037 (14)	0.0068 (12)	−0.0010 (13)

Geometric parameters (Å, º)

S1—C1	1.629 (3)	C6—H6A	0.9900
S2—C2	1.635 (3)	C6—H6B	0.9900
N1—C2	1.384 (3)	C7—C12	1.388 (4)
N1—C1	1.390 (3)	C7—C8	1.394 (4)
N1—C6	1.473 (3)	C8—C9	1.390 (4)
C1—C4	1.469 (3)	C8—H8	0.9500
C2—C3	1.477 (3)	C9—C10	1.382 (5)
C3—C5	1.384 (4)	C9—H9	0.9500
C3—C4	1.399 (4)	C10—C11	1.374 (5)
C4—C5ⁱ	1.388 (3)	C10—H10	0.9500
C5—C4ⁱ	1.388 (3)	C11—C12	1.388 (4)
C5—H5	0.9500	C11—H11	0.9500
C6—C7	1.515 (4)	C12—H12	0.9500
C2—N1—C1	112.3 (2)	N1—C6—H6B	108.9
C2—N1—C6	124.4 (2)	C7—C6—H6B	108.9
C1—N1—C6	123.1 (2)	H6A—C6—H6B	107.7
N1—C1—C4	106.0 (2)	C12—C7—C8	119.4 (3)
N1—C1—S1	125.63 (19)	C12—C7—C6	120.6 (2)
C4—C1—S1	128.3 (2)	C8—C7—C6	120.0 (2)
N1—C2—C3	105.8 (2)	C9—C8—C7	120.1 (3)
N1—C2—S2	127.14 (19)	C9—C8—H8	120.0
C3—C2—S2	127.06 (19)	C7—C8—H8	120.0
C5—C3—C4	122.7 (2)	C10—C9—C8	119.7 (3)
C5—C3—C2	129.4 (2)	C10—C9—H9	120.1
C4—C3—C2	107.9 (2)	C8—C9—H9	120.1
C5ⁱ—C4—C3	122.5 (2)	C11—C10—C9	120.5 (3)
C5ⁱ—C4—C1	129.6 (2)	C11—C10—H10	119.8
C3—C4—C1	107.9 (2)	C9—C10—H10	119.8
C3—C5—C4ⁱ	114.8 (2)	C10—C11—C12	120.2 (3)
C3—C5—H5	122.6	C10—C11—H11	119.9
C4ⁱ—C5—H5	122.6	C12—C11—H11	119.9
N1—C6—C7	113.4 (2)	C11—C12—C7	120.1 (3)
N1—C6—H6A	108.9	C11—C12—H12	119.9
C7—C6—H6A	108.9	C7—C12—H12	119.9
C2—N1—C1—C4	−0.2 (3)	S1—C1—C4—C5ⁱ	−0.3 (4)
C6—N1—C1—C4	175.6 (2)	N1—C1—C4—C3	−1.2 (3)
C2—N1—C1—S1	−178.89 (19)	S1—C1—C4—C3	177.4 (2)
C6—N1—C1—S1	−3.1 (3)	C4—C3—C5—C4ⁱ	−0.3 (4)
C1—N1—C2—C3	1.5 (3)	C2—C3—C5—C4ⁱ	−180.0 (2)

C6—N1—C2—C3	−174.3 (2)	C2—N1—C6—C7	−108.7 (3)
C1—N1—C2—S2	−177.3 (2)	C1—N1—C6—C7	76.0 (3)
C6—N1—C2—S2	7.0 (4)	N1—C6—C7—C12	64.7 (3)
N1—C2—C3—C5	177.5 (3)	N1—C6—C7—C8	−116.7 (3)
S2—C2—C3—C5	−3.8 (4)	C12—C7—C8—C9	0.0 (4)
N1—C2—C3—C4	−2.2 (3)	C6—C7—C8—C9	−178.7 (3)
S2—C2—C3—C4	176.5 (2)	C7—C8—C9—C10	0.1 (5)
C5—C3—C4—C5^i	0.3 (4)	C8—C9—C10—C11	−0.3 (5)
C2—C3—C4—C5^i	−180.0 (2)	C9—C10—C11—C12	0.4 (5)
C5—C3—C4—C1	−177.6 (2)	C10—C11—C12—C7	−0.3 (5)
C2—C3—C4—C1	2.1 (3)	C8—C7—C12—C11	0.1 (4)
N1—C1—C4—C5^i	−179.0 (3)	C6—C7—C12—C11	178.8 (3)

Symmetry code: (i) −x+2, −y+1, −z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6*B*···S2	0.99	2.75	3.208 (3)	109
C6—H6*B*···Cg1^{ii}	0.99	2.66	3.498 (3)	142

Symmetry code: (ii) x, y+1, z.